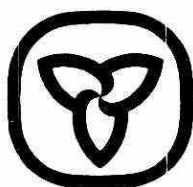


DETERMINATION OF EXTRACTABLE
COPPER, NICKEL AND ALUMINUM
IN SLUDGE - AMENDED MINE TAILINGS

February, 1981

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Deputy Minister

DETERMINATION OF EXTRACTABLE COPPER, NICKEL AND ALUMINUM
IN SLUDGE - AMENDED MINE TAILINGS.

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Ontario Ministry of the Environment

February, 1981

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ABSTRACT

Samples of sewage sludge amended tailings from Inco Metals Company, Sudbury were analyzed for acidified ammonium acetate extractable Cu, Ni and Al by Inco and the Ministry of the Environment Sediment and Sewage Laboratory. A mechanical extractor was used at MOE compared with a shake test at Inco. DTPA was also evaluated at MOE as an alternate extractant for Cu and Ni and KCl and CuCl_2 for Al. Correlation was satisfactory between the two laboratories for ammonium acetate extractable Cu and Ni with more metal extracted by the mechanical extractor. There was also a satisfactory relationship between DTPA extractable metals at MOE and Inco's ammonium acetate data.

Ammonium acetate appeared to be less satisfactory than KCl as a measure of soluble plus exchangeable Al. CuCl_2 yielded higher results, probably because of the release of organo-Al. There was some indication that the difference between CuCl_2 and KCl extractable Al could be related to organic matter content.

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I - INTRODUCTION

A series of mine tailings samples were analyzed by the Environmental Control Department of Inco Metals Company for selected extractable metals. The data generated was expected to complete the study by Laurentian University staff, under the sponsorship of the Ministry of the Environment, of factors affecting the development of vegetative cover on a tailings site in the Sudbury area. Most of the samples had been collected in 1974.

A shake test procedure with acidified ammonium acetate as extractant was used by Inco at the request of MOE to provide compatability with earlier data obtained by the MOE Sediment and Soils Laboratory.

Extracts were analyzed by Inco for copper, nickel, zinc and aluminum. These metals were thought to be most significant to the study. The presence of appreciable concentrations of these metals in extractable form had been established by the earlier analyses at MOE. It is also well known that these metals can be toxic to plants under some conditions. Soluble aluminum is thought to have special significance under acidic conditions (Darcel, 1980).

Ammonium acetate, acidified to pH 4.8, had been selected for the earlier study, since this extractant has been in popular use in a "shake test" for "available" metal determinations in soils for many years (Canada Soil Survey, 1976). More recently DTPA (diethylene triamine penta-acetic acid) has become widely used in plant uptake studies of toxic metals.

Acidified ammonium acetate has been used for exchangeable aluminum, although KCl is in more general use (Black, 1965). There is some evidence that exchangeable plus organo-aluminum, and other forms extractable with CuCl_2 , may have significance in acid soils (Juo and Kamrath, 1979).

A Concept Engineering mechanical vacuum extractor had been evaluated at the Sediment Laboratory for DTPA soil extraction studies (Mo, 1979). It was planned, therefore, to extend the evaluation of the extractor to mine tailings and other extractants.

Advantage was taken of the Inco data to reduce the number of samples to be tested at MOE. Samples were selected initially to represent low and high concentrations of each extracted metal as determined by Inco; in the second phase of the study "fill-in" samples of intermediate concentration were selected. It was unfortunate that for some samples there was insufficient material for all tests.

The same metals were determined in a few samples following digestion with hot HCl/HNO_3 to obtain an indication of the total metal content potentially available. A few samples were tested for pH and loss on ignition to assist in interpretation of the data.

Because of manpower and funding limitations and pressure of routine work the study "dragged" over a prolonged period. In addition, it was not possible to undertake a thorough statistical inter-comparison of methods or assessment of metal extractability. It was hoped, however, that the results would assist in determining the direction of future studies.

II - METHODS

In the procedure followed by Inco air-dry samples were mixed in a 1:4 ratio with 1N ammonium acetate, which had been adjusted to pH 4.8 with acetic acid, and shaken for thirty minutes on a wrist action shaker. The extract was then analyzed for the metals under study using atomic absorption spectrophotometry (AAS). Practice at MOE had been to digest the extracts with HCl/HNO_3 prior to analysis; Inco, however, found this step to be unnecessary providing standards were made up in ammonium acetate.

A mechanical vacuum extractor (using syringes) developed for the determination of Cation Exchange Capacity and the major

exchangeable cations (Soil Survey Laboratory, 1979) was used by the MOE Sediment and Sewage Laboratory. Various ratios of solid : liquid were evaluated. Extracts were weighed rather than measuring volume to improve accuracy.

Comparisons were made between acidified ammonium acetate and 0.005 N DTPA as extractants for Cu and Ni. Extractable Zn was also studied initially; unfortunately, this study was discontinued due to contamination attributed to the presence of Zn in the plastic syringe plungers. There was also a significant blank for Al; this was not considered to be as serious as for the Zn blank because concentrations of Al in the extracts were higher relative to the blank.

The study with ammonium acetate extraction at MOE was extended to Pb, Cd and Mn.

In the mechanical vacuum extractor 10g initially (later 2.5g) of the air-dry tailings were placed in the upper syringe above a filter pulp pad and extracted for six hours (overnight in later tests) with different ratios of solid : ammonium acetate extractant. Tests were conducted with 1:4 (10g/40mL), 1:12 (2.5g/30mL) and 1:15 (2.5g/40mL) ratios. Extracts collected in the lower syringes were weighed and aliquots digested (or taken as-is) and analyzed by AAS. In the earlier tests, the 10g of tailings was mixed with Celite to assist filterability. This was later found unnecessary and the practice was discontinued.

Overnight extractions with DTPA were also conducted experimenting with various ratios of solid : extractant, ranging from 1:24 to 1:100 using a constant volume of extractant (60mL).

Samples were analyzed for extractable Al at MOE using the mechanical extractor. Extractants evaluated were ammonium acetate (pH 4.8), 1 N KCl and 1 N CuCl_2 . The sample size used in the initial tests was 10g, extracted overnight with 40 mL (1:4 ratio). In later work 3g:40mL (1:13) was used. The difference between CuCl_2 and KCl extractable Al was plotted against Loss on Ignition.

All extracts were analyzed by AAS using a Varian Model 1250 or Perkin-Elmer Models 503 or 5000. A comparison was made between

concentrations obtained on digested (HCl/HNO_3) and undigested ammonium acetate extracts to verify Inco's findings. A similar comparison was made for DTPA. Extracts in CuCl_2 and KCl were analyzed for Al without digestion, using routine standards made up in HNO_3 .

Some samples were analyzed for pH in 0.01 M CaCl_2 (Canada Soil Survey, 1976). Loss on ignition was determined at 475°C . Some samples were analyzed for hot acid extractable metals using the routine HCl/HNO_3 digestion procedure (Darcel, 1975).

III - RESULTS

1 - Extractants for Cu, Ni and Zn

Ammonium Acetate

The Inco data indicated a wide range of extractable metals.

TABLE I

Extractable metals (Inco)

	Range - $\mu\text{g/g}$	me/100g
Cu	5 - 178	.16 - 5.5
Zn	1 - 115	.03 - 3.4
Ni	1 - 79	.03 - 2.7

Regressions - MOE on Inco

Concentrations of extractable metals were compared for the same solid : extractant ratio (1:4) for the Inco shake test and MOE extractor.

Copper

Correlation was satisfactory ($r = 0.952$) for 16 data sets. There was some bias towards higher results (17.3%) by the MOE method ($\bar{X}_{\text{MOE}} = 76.68 \mu\text{g/g}$; $\bar{X}_{\text{INCO}} = 63.38 \mu\text{g/g}$). The slope of 0.799 was significantly different from 1.00. No data sets were rejected (Figure I).

Nickel

The correlation was slightly better than that for copper ($r = 0.965$) for 16 points with better agreement than for Cu between mean values (21.96 and 23.00 $\mu\text{g/g}$) for MOE and INCO, respectively. The slope was also closer to 1.00 (1.096). As for copper, no data points had to be rejected. (Figure I)

Zinc

The preliminary data with 9 sets appeared promising in spite of the contamination problem. There was an indication of a relatively strong bias towards higher results (26%) by MOE ($\bar{X}_{\text{MOE}} = 16.87 \mu\text{g/g}$; $\bar{X}_{\text{INCO}} = 12.44 \mu\text{g/g}$) and a marked deviation of slope from 1.00 (0.617). Unfortunately, there was an absence of data points in the middle range, tending to invalidate the correlation (Figure III).

Solid : Extractant Ratio - Ammonium acetate

Strong correlations and a linear relationship were obtained for Cu between 1:4 and 1:12 (R_4 vs R_{10} of Figure IV) and 1:4 and 1:16 (Figure VII) with more copper extracted at the 1:16 ratio. (R_{10} refers to ratio of solid to extract).

There was also a strong correlation for Ni (Figure V).

There were an inadequate number of observations poorly distributed for Zn (and a blank problem) to draw a firm conclusion. There was, however, an indication of an increase in Zn extracted at 1:12 compared with 1:4 (Figure VI). When the values for Cu and Ni extracted at different solid : extractant ratios for specific samples are expressed graphically (Figure VIII) there is an indication that even at 1:16 ratio extraction is not quite complete for most samples, particularly for higher concentrations of extractable metal.

Digested versus undigested

Copper

Only 5 data sets were used. However, they covered a wide range of concentrations. There was a strong correlation ($r = 0.989$), with a bias towards higher results (6.3%) on digested samples

($\bar{x}_{\text{DIG}} = 72.12 \text{ } \mu\text{g/g}$; $\bar{x}_{\text{UNDIG}} = 67.84 \text{ } \mu\text{g/g}$) and a slope of 0.87 (Figure IX).

Nickel

A strong correlation ($r = 0.9997$) was indicated for the 5 data sets. Unfortunately, they were not well distributed over the range of concentrations. There was little bias and the slope was close to 1.00 (Figure X).

DTPA Extractions

Regressions MOE on Inco Ammonium Acetate

Comparisons were made between Inco shake test data for ammonium acetate extractable metals and MOE mechanical vacuum extractor results for DTPA.

Copper

For 24 data sets there was a strong correlation ($r = 0.968$), but a 27% bias towards higher results by DTPA ($\bar{X}_{DTPA} = 60.84 \mu\text{g/g}$; $\bar{X}_{AmAc} = 47.88 \mu\text{g/g}$), and a slope of 1.188, significantly different from 1.00 (Figure XI).

Nickel

For 25 data sets, the correlation was weaker than for copper ($r = 0.901$) due probably to increased variability at higher concentrations. Little bias was evident and the slope was close to 1.00 (Figure XII).

Solid : extractant ratio

Relationships between extractable Cu and Ni at high solid : extractant ratios for several tailings samples were investigated (Figures XIII, XIV). The results indicated that maximum extraction occurred at higher ratios for higher levels of extractable metals.

Digested versus undigested

Comparison of results in spot checks for digested DTPA extracts versus As-Is extracts (using standards made up in DTPA and in HNO_3) demonstrated absence of bias between procedures. There was insufficient data to calculate regressions.

2 - Extractants for Aluminum

Ammonium acetate - Inco versus MOE

A few samples (6) were compared for ammonium acetate extractable Al by shake test at Inco and extractor at MOE (both at 1:4 ratio). There was some indication of a relationship for a cluster of 3 points at the 10 µg/g level. However, the data was poorly distributed and there was evidence of "fliers" (Figure XV).

Ammonium acetate (Inco) versus DTPA

DTPA extracted very little Al with little relationship with ammonium acetate extractable Al (up to 5 µg/g for ammonium acetate extractable Al ranging from 5 to 25 µg/g). A value of 8 µg/g Al by DTPA corresponded with 60 µg/g by ammonium acetate.

Ammonium acetate versus KCl

There was evidence of a non-linear relationship between ammonium acetate and KCl extractable Al using the mechanical extractor (Figure XVI).

Extractant Ratio for Ammonium acetate

The effect of solid : extractant ratio on ammonium acetate extractable Al was checked for 1:4 and 1:12 ratios.

A bad "flier" and only one data point at a higher concentration level negated an attempt to obtain a correlation for Al. There was some indication of a relation between 1:4 and 1:12 ratios for 15 - 35 µg/g Al (1:4) and 30 - 45 µg/g (1:12) with more Al extracted at the higher ratio (Figure XVI).

Extraction with KCl and CuCl₂

Samples were extracted overnight in the mechanical extractor with KCl and CuCl₂ at 1:13 solid : extractant ratio at a three month interval to check on reproducibility. Consistent extractions were obtained for two sets of extractions with KCl (Figure XVIII) run on August 15 and December 17, 1980. Less consistent data was obtained for CuCl₂ (Figure XIX).

Higher values for extractable Al were obtained for CuCl₂ compared with KCl but there was little correlation. Better agreement was obtained between the difference in extractable Al between CuCl₂ and KCl and Loss on Ignition (Figure XX).

TABLE II

Extractable Aluminum $\mu\text{g/g}$ Vacuum Extractor

<u>Inco Sample No.</u>	<u>KCL</u>	<u>CuCl_2</u>	<u>Ammonium Acetate pH 4.8</u>
242	6.4 , 5.5 [*]	(26) , 52	
259	.65, .54	56 ,	
284	39 , 36	57	63 ,
866	111 , 110	89 , 140	95 , 70
878	120 , 110	140 , 100	92 , 94
883	<2. , 2.3	(41) , 100	18
902	35	91 , 88	71
932	26 , 28	120 , 100	30 , 51
962	16 , 18	82	49
1119	2.5	36	45
1138	12 , 13	87 , 63	60
1186	3.6, 2.9	79 , 78	34

* Repeat tests run on different days (15/8/80 and 17/12/80)

Figures is parentheses discarded

Inco - Ammonium Acetate pH 4.8 Shake test

	$\mu\text{g/g}$	m.e./100g
Range	<5 - 65	<.05 - .71

3 - pH Measurements

pH was measured in 0.01 M CaCl_2 on a few selected samples.
The samples were acidic.

TABLE III

<u>Inco Sample no.</u>	<u>pH CaCl_2</u>
235	5.5
242	4.3
1119	4.7
1186	4.4
307	5.3
883	5.7

4 - Loss on Ignition

TABLE IV

<u>Inco Sample no.</u>	<u>Loss on Ignition %</u>
902	2.5
866	0.9
259	3.8
878	1.1
962	1.8
1138	3.5
932	2.8

5 - Hot Acid Digestion

Hot acid (HCl/HNO_3) digestion of selected samples indicated relatively high concentrations of Cu and Ni in all samples tested. Al was also high (in spite of incomplete extraction).

TABLE V

Metal Concentrations $\mu\text{g/g}$

Inco Sample no.	Cu	Ni	Al x 1000	Zn
887	640	390	21	82
913	810	640	21	73
920	310	580	33	64
955	470	350	24	59
1095	670	380	20	66
1096	350	190	20	44
1101	740	630	24	120
1102	810	530	27	82
1131	780	690	21	83
1162	660	470	25	110

IV - DISCUSSION

Caution must be exercised in attempting to draw firm conclusions for the data. The samples were "old" by the time of the extraction tests in 1979, having been stored air-dry since 1974. Storage may have affected extractability of metals. It is suggested, however, that the relative extractability of samples stored for the same length of time will not have been significantly affected.

The extractants used in this study were developed originally for agricultural soils. DTPA has been used, however, in coal mine soil reclamation studies in the Northern Great Plains of the United States (Gough et al, 1980).

Base metal sulphides have a very different composition to soils. Iron, sulphide and trace metal concentrations are much higher than in typical soils (Hawley, 1980). Reactions between the minerals in the tailings and the extractants can be expected to be different to those occurring in soils. The high sulphide

content is of interest in that it would tend to generate acid and solubilize metals.

Data obtained for agricultural soils and crops may, therefore, have little relevance to the tailings - vegetation study. Indeed, the results may be applicable only to this specific eco-system.

It can be assumed that most of the extractable metals found in this study were derived from the tailings. However, consideration must also be given to the contribution of the sewage sludge both as an initial source of metal and its possible effect on mobilization of metals.

1 - Extractants for Cu, Ni and Zn

Ammonium Acetate

More Cu, Ni and Zn were extracted by the mechanical vacuum extractor than the shake test, particularly at higher extractant : solid ratios. This can be expected as the solid is continually leached with fresh extract and there is minimal re-adsorption. However, since there is a good correlation, results can be related. The values obtained by the Inco shake test may be about two times low for higher levels of extractable Cu (and possibly Zn) but could represent the relatively easily extractable fraction.

It is important for the mechanical extractor that sample size not be made too small because this increases the chance of by-passing and incomplete leaching unless a wide ratio of solid to extractant is used.

In the operation of the mechanical extractor, some extractant liquor is held in the sample, filter pulp (and Celite, if used) against the suction force drawn by the lower syringe. It has to be assumed that this liquor contains negligible metal of interest as the calculation of extracted metal is based solely on the concentration in extracted liquor in the lower syringe. If the extraction is incomplete (too narrow a ratio between solid and extractant) there may be a significant amount of metal trapped in the sample; hence low values for extracted metal. This situation does not occur with the shake test as all

the liquor is available for test.

Experience with the equipment indicated that 2.5 - 3.0 g was a practicable sample size for a 1:16 solid : extractant ratio with ammonium acetate.

The problem of Zn contamination was attributed to the presence of the metal in the plastic plungers in the disposable syringes. A prototype Zn-free plunger was found to be satisfactory. Replacement plungers are being purchased.

The Al contamination problem was not completely resolved at the time. The Celite filter aid was suspect and its use was discontinued in later work.

Analysis of undigested ammonium acetate extracts by AAS is satisfactory, particularly since it results in appreciable savings in time. There appeared to be some bias between results for digested and undigested extracts. This may have been due to the use of standards in dilute acid rather than in ammonium acetate in the MOE study.

DTPA

A procedure for the use of DTPA with the mechanical extractor had been developed in our laboratory (Mo, 1979). Extracts could be analyzed using routine standards made up in HNO_3 . This was the preferred method as standards made up in DTPA tended to deteriorate with time.

There was evidence from the present study that the minimum solid : extractant ratio for complete removal of extractable metal with DTPA varies with element and concentration of extractable metal.

It appears that both DTPA and ammonium acetate at pH 4.8 are promising extractants for at least some toxic metals in the tailings samples studied.

DTPA may be preferred to ammonium acetate in AAS analysis because of the lower solids content of the extract and hence

reduced tendency to plug nebulizer and burner.

The significance of the differences in concentration of metals released by DTPA compared with acidified ammonium acetate for the Inco tailings has not been established. DTPA has more generally been used on neutral to alkaline soils. The fact that the reagent is buffered to pH 7.3 compared with the pH 4.8 of the ammonium acetate may be important.

In the coal mine soil reclamation study of the Northern Great Plains (Gough et al, 1980) pH ranged from 6.2 - 8.2. Concentrations of DTPA extractable Cu were lower than for the Inco tailings (0.1 - 1.2 $\mu\text{g/g}$) for total Cu ranging from 3 - 30 $\mu\text{g/g}$ in the A - horizon

The finding that significantly more Cu (but not Ni) was extracted by DTPA than ammonium acetate at pH 4.8 with the Inco tailings indicates that Cu does not become "available" only from water soluble and exchange positions. DTPA is well known as a complexing agent freeing metal associated with the organic fraction. Transfer from the organo-metallic state may, therefore, also be an important mechanism in amended tailings for Cu but not for Ni.

Concentrations of extractable metal were high in several of the samples analyzed. The results obtained by Inco for extractable Cu, Ni and Zn may be relevant with respect to toxicity and plant growth and metal uptake on the tailings site.

It is of interest that in spite of the apparent high concentrations of potentially toxic metals plant cover became established on the tailings. This could suggest that the metals were at least partially bound in less toxic complexes. It could also indicate that very hardy plant species were selected and/or growth is below maximum (but satisfactory).

It may be important to differentiate between the easily releasable fraction of toxic metal (possibly 1:4 tailings : extractant ratio) and the ultimate pool (above the minimum ratio for no significant increase in extractable metal). The minimum

ratio will vary with element, its concentration and type of extractant. Such a differentiation might assist in interpreting toxicity and metal uptake effects. Two stage extractions would be required. DTPA extractable Fe and Mn may also have some effect on the uptake of other metals. Unfortunately, they were not determined in the present study.

2 - Extractants for Aluminum

The Inco results for extractable Al may be of use although it could not be related as closely as the other metals to MOE data.

There is some indication from the lack of correlation between shake test and extractor for extractable Al that ammonium acetate may not be a very satisfactory extractant for Al. Juo and Kamrath (1979) came to the same conclusion in contradiction with McLean (1965) who found the reagent satisfactory for very acid soils. The data used in our study was limited, however, and the problem with Al blanks with the extractor method probably contributed to the poor relationship. There were also inconsistencies in attempting to determine relationships for Al extracted at different solid : liquid ratios in the mechanical extractor using ammonium acetate (Figure XVII).

Acceptable results were obtained using KCl in the mechanical extractor with good agreement between different runs. There was also some indication of a non-linear relationship with ammonium acetate extractable Al. At the mid-range approximately similar amounts of Al were extracted by the two reagents. This can be expected on the basis that both extractants should provide (at low pH) measure of exchangeable Al (plus minor amounts of water soluble Al).

The data for CuCl_2 extractable Al was more variable than for KCl. No explanation can be given at this time except for the possibility of analytical problems such as interference in nebulization due to the high salt content, presence of organics, high concentration of Cu or omission of La or K as suppressants. Incomplete extraction was also a possibility.

It has been shown that Cu up to at least 500 mg/L resulted in a small increase (about 12 - 14%) in measured value for 1 mg/L Al with and without La addition (Webber, 1974). It is usually recommended that 1000 mg/L K be added as a suppressant prior to analysis of Al by AAS; this was omitted in the present study with CuCl_2 because there was some concern over increasing the already high salt content. In addition, it was demonstrated for a number of tailings extracts analyzed by AAS with and without 1000 mg/L K that there was no significant difference in measured value for Al concentration. Indeed, the addition of K appeared to be undesirable; a "flash-back" at the P-E 5000 nebulizer occurred while running the extracts with added K. In future work the CuCl_2 should be diluted prior to analysis and the nebulizer and burner assembly adequately rinsed with distilled water between samples.

The KCl and CuCl_2 extracts were not digested prior to AAS analysis. This may have had some effect on the variability of the data, particularly for CuCl_2 (expected to extract organic in addition to exchangeable Al).

Extractions may not have been complete, even at 1:13 solid : extractant ratio, particularly for CuCl_2 . Juo and Kamrath (1979) had used a 1:10 ratio in a shake test; they required 3 or 4 successive extractions.

The results for KCl extractable Al may be slightly high due to analytical bias. No La was added prior to AAS in our study. Webber (1974) showed that in 1 N KCl Al recovery was 115% and 136% for 1 mg/L Al with and without, respectively, addition of 2000 mg/L La. Countering this possible enhancement, however, is the suggestion that extraction may not have been complete, as suggested above.

CuCl_2 extracted more Al than KCl in most of the tailings samples indicating the presence of a potential source of soluble Al in OH-Al polymers and/or organo-Al complexes. The presence of the latter form is also suggested from the plot of $\text{Al}_{\text{CuCl}_2} - \text{Al}_{\text{KCl}}$ against Loss on Ignition (a measure of organic content).

Lime addition rates designed to raise the pH to optimum (pH 6.5) will be inadequate if based solely on KCl exchangeable Al, rather than on total reactive Al (CuCl_2 exchangeable).

3 - pH and Exchange Acidity

The Al concentration of soil solution is thought to be a measure of aluminum toxicity potential for plants (Brenes and Pearson, 1973). It has been observed that soluble and exchangeable Al in soils generally increase with decrease with pH (Black, 1957), especially below pH 5 (Juo and Kamrath, 1979). pOH is significant relative to the solubility of $\text{Al}(\text{OH})_3$ (Clark, 1966). Acid injury, as indicated by root growth of test plants was noted at "critical" pH values ($\text{pH}_{(\text{H}_2\text{O})}$ and $\text{pH}_{(\text{KCl})}$) of about 5.0 and 4.5, respectively for chloritized 2:1 mineral Andosols of north-eastern Japan (Saigusa et al, 1980). On the other hand, for Andosols with allophane - imogolite minerals there was no critical pH and no significant effect on root growth even at $\text{pH}_{(\text{H}_2\text{O})}$ of 4.6. Associated clay minerals are important, therefore, in relation to critical pH.

Recently, Saigusa et al (1980) found that values of exchange acidity determined by titration of KCl soil extract (soil: 1 N KCl of 1:2.5) with 0.1 N NaOH correlated closely with total exchangeable (KCl extractable) Al and was a realistic measure of aluminum toxicity in acid Andosols.

In the present study pH was measured in 0.01 M CaCl_2 following the procedure recommended by the Canada Soil Survey (1976). Differences have been noted comparing pH in CaCl_2 compared with pH in water but this was not checked for the tailings samples. It is expected that the pH in CaCl_2 and KCl would be similar.

The pH values obtained for the few samples tested in the present study indicate that the tailings are moderately acidic ($\text{pH}_{\text{CaCl}_2}$ 4.3 - 5.7). The acid effect can be attributed to both the H^+ ion and exchangeable Al. Toxicity effects due to $\text{H}^+ + \text{Al}$ could be a problem (Darcel, 1980); however, this factor could be moderated if much of the Al is in organic complexes, as suggested by the data.

Measurement of aluminum saturation (of the exchange complex) and exchange acidity by titration of the KCl extract could have proved useful. Oxalate extractable "free" Al may have relevance (Clark, 1966).

Promising results have been obtained using silver thio-urea as a single extraction method for measuring exchangeable cations in soils including exchange acidity (Al + H) and cation exchange capacity (Pleysier and Juo, 1979). The method may have application to mine tailings and northern acid soils.

4 - Loss on Ignition - Organic Content

The Loss on Ignition at 475°C is a measure of organic matter content. The values obtained for the few samples analyzed indicated a variable low content by soil standards. At least some of this organic matter was contributed by the sewage sludge addition. The physico-chemical properties of the organic content in this material are somewhat dissimilar to normal soil humus.

The apparent relationship between LOI and organo-Al is of interest. It is possible that the relationship would be stronger if total carbon (by LECO, CHN analyzer or Walkley-Black method) rather than LOI was used.

5 - Hot Acid Digestion

It is well known that digestion of a sediment or soil with HCl/HNO₃ does not release all the metal into solution (Darcel, 1975). Silicates are only partially dissolved; hence metals locked within the alumino-silicate structure will not be released. However, for metals such as Cu, Zn and Ni, most of the metal content is released. On the other hand, only a small fraction of the total Al is released.

The range in concentrations of extractable Cu, Ni and Zn as determined by Inco (Table I), or these values adjusted by a 2X factor to allow for concentrations ultimately extractable by weak extractants using high tailings : extractant ratio in the mechanical extractor, are well below the concentrations determined following hot acid digestion (Table VI), particularly for Cu and Zn. A much smaller fraction of the Al is released even with CuCl₂ (Table II).

Under highly acidic natural conditions more metal may be released. The concentrations obtained by HCl/HNO_3 digestion could then be significant as total potentially available toxic metals.

6 - Inco Tailings Program

The results of the study indicate significant concentrations of potentially toxic metals and pH values which could be critical for sensitive plants. Organic matter content (indicated by Loss on Ignition) was low compared with levels expected for a fertile soil. It is of interest, however, that in spite of the above negatives plant cover was established on the tailings.

Inco has followed a program of commercial fertilizer and lime addition over the past seven years and a satisfactory grass cover has been maintained. It would be useful if a carefully selected set of soil and vegetation samples were collected from the site and analyzed for metals (hot acid extractable for vegetation and soil, plus extractable metals for soil samples). pH, exchange acidity plus aluminum, and Loss on Ignition should be determined on the soil samples.

If the soil is found to be acidic in spite of the liming it might be useful to look for signs of acid damage to roots. Lime Requirement should also be determined. It is suggested that if the presence of a potentially reactive Al pool is again found ($\text{Al}_{\text{CuCl}_2} - \text{Al}_{\text{KCl}}$) lime addition rates based on Lime Requirement will be low. An Acid Potential effect from acid generated during the oxidation of residual sulphide in the tailings will also contribute to an under-estimate of the lime requirement.

If the pH of the rooting medium becomes strongly acidic it can be expected that toxicity effects due to soluble Al and exchange acidity will be compounded by the contributions to toxicity of high concentrations of other potentially toxic metals such as Cu and Zn.

The results of the proposed study would be of assistance in other tailings - vegetation and acid soil toxicity and metal uptake studies.

V - CONCLUSIONS

- 1 - Ammonium acetate (pH 4.8) extractable data obtained by shake test at Inco is satisfactory for Cu, Ni and probably Zn but there are reservations as to its applicability to Al. Higher concentrations were obtained for ammonium acetate using the mechanical extractor indicating that the shake test values may be slightly low, relative to the amounts ultimately extractable.
- 2 - DTPA was a more powerful extractant for Cu than ammonium acetate (pH 4.8). On the other hand, the two extractants were similarly effective for Ni. This could suggest (as has been shown in other studies) that soluble organic complexes can be formed fairly readily with Cu but not for Ni. There is supporting evidence in the relative effects of solid : extractant ratio for Cu and Ni. For lower concentrations (40 µg/g) of DTPA - extractable Cu extraction was complete.
- 3 - There are indications of significant concentrations of exchangeable Al and potentially active pools of Al in organic complexes in some samples.
- 4 - The mechanical extractor has an advantage over the shake test in terms of reproducibility of extracting conditions and minimizing re-adsorption; however, the shake test is also satisfactory.
- 5 - Solid : extractant ratio is important for the mechanical extractor with respect to completion of extraction.
- 6 - Digestion of ammonium acetate or DTPA extracts prior to AAS analysis for metals is not necessary, at least for the type of samples under study.
- 7 - Ammonium acetate, pH 4.8, and DTPA both appear to be suitable as extractants for Cu and Ni (and probably Zn). Similarly, KCl is satisfactory for exchangeable Al and CuCl_2 is useful for determining exchangeable + organic Al.

VI - RECOMMENDATIONS

- 1 - The vegetated Inco tailings site should be re-sampled to determine the effect of the time factor (1974-1981), liming and fertilization on the availability of metals, acidity effects and metal uptake by plants. Lime requirement should be assessed taking into account organo-Al and acid potential.
- 2 - If an acidic condition is indicated, parameters measured in the present study should be supplemented with pore-water analysis, exchange acidity, lime requirement, total sulphur (for acid potential) and possibly oxalate extractable aluminum and aluminum saturation. Extraction tests should be designed to attempt to determine short and longer term effects. If the tailings are no longer acidic, measurement of extractable metals would still be of interest but not as critical.
- 3 - The mechanical extractor, fitted with zinc-free plungers, should be used for the extraction tests. Measurements should again be made for Cu, Ni and Zn using ammonium acetate (pH 4.8) and DTPA in multiple stage extractions or a range of tailings : extractant ratios. Extractable Fe and Mn should also be measured.
- 4 - The preliminary study on exchangeable and organo-Al, and relationships with total organic matter, should be followed up on fresh samples. The test procedure for CuCl_2 should be modified to include a wider solid : extractant ratio and digestion and dilution of extracts prior to AAS analysis. Use should be made of the KCl extract for the measurement of exchange acidity. Silver thio-urea should also be evaluated as an extractant for Al and exchange acidity.
- 5 - Measurements should be made of particle size distribution to assist in the interpretation of the data. The clay-size fraction in the exchange complex should be identified in terms of mineralogical composition to assist in interpreting critical pH conditions for root growth.
- 6 - The effects of fertilizer addition should be investigated, particularly the addition of phosphate in relation to its availability to the plants.

- 7 - Studies should be undertaken of the effect of sewage sludge on the mobilization and possibly detoxification of metals in tailings; particularly under acidic conditions.

VII - ACKNOWLEDGEMENTS

The assistance of Mr. H. R. Butler and Mr. D. Maskery of the Environmental Control Department, Inco Metals Company, Sudbury in providing laboratory services at no charge and supervising the analysis of the samples is greatly appreciated. Mr. L. W. Fitz, District Officer, North-eastern Region, Ontario Ministry of the Environment and Mr. T. van Rossum, Environmental Officer, were instrumental in arranging Inco support. Extractions at MOE were conducted by Mr. F. Mo and Miss E. Seunarine. Mrs. D. Chan graciously "squeezed-in" AAS measurements on the extracts between routine runs. Appreciation is also extended to Dr. B. Loescher and Ms. A. Bohdanowicz for reviewing the manuscript.

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IX APPENDICES

1. INCO AMMONIUM ACETATE SHAKE TEST

COPPER

NICKEL

ZINC

ALUMINUM

INCO METALS COMPANY

Copper Cliff, Ontario P0M 1N0

Environmental Control
Department
Ontario Division

March 19, 1979.

Ministry of the Environment,
Industrial Abatement,
Regency Mall,
469 Bouchard Street,
Sudbury, Ontario.

Attention: Mr. L. W. Fitz, P. Eng.,
District Officer


Re: MOE/Laurentian University
Tailing Area Samples

Dear Mr. Fitz:

Two copies of the analytical results of tailing area soil samples are attached. This completes the work we were requested to do for your Ministry.

I trust you and your colleagues will find this work satisfactory. However, if there are questions regarding the analytical results, please contact our Mr. David Maskery at 682-4870.

Yours very truly,



H. R. Butler, P. Eng.,
Supervisor,
Environmental Control.

HRB:jv

MAR 16 1979

INCO Form 78-R • Revised 5-73

Process Technology • Analytical Services

MISCELLANEOUS ASSAY REPORT

submitted by <u>H.R. BUTLER</u>	charge number <u>18163-1110</u>	date <u>SEPTEMBER 8, 1978</u>
department <u>ENVIRONMENTAL CONTROL</u>	location	
program description <u>VOLUNTARY EMISSION REDUCTION</u>		

lab no.	sample description	analysis required <u>Soluble Cu, Ni, Zn and Al ANALYSES OF SOIL</u> <u>SAMPLES LEACHED WITH AMMONIUM ACETATE (ADJUSTED</u> <u>TO pH 4.8 WITH</u> <u>ACETIC ACID)</u>							
		PPM							
		Cu	Ni	Zn	Al				
	<u>MOE./LAURENTIAN</u> <u>TAILINGS AREA</u> <u>SAMPLES</u>								
	<u>217 Soil</u>	<u>19.</u>	<u>6.</u>	<u>5.</u>	<u><5.</u>				
	<u>218 "</u>	<u>8.</u>	<u>3.</u>	<u>3.</u>	<u>25.</u>				
	<u>223 "</u>	<u>69.</u>	<u>30.</u>	<u>4.</u>	<u><5.</u>				
	<u>224 "</u>	<u>37.</u>	<u>4.</u>	<u>2.</u>	<u><5.</u>				
	<u>229 "</u>	<u>10.</u>	<u>8.</u>	<u>1.</u>	<u>13.</u>				
	<u>230 "</u>	<u>7.</u>	<u>2.</u>	<u>2.</u>	<u>25.</u>				
	<u>235 "</u>	<u>128.</u>	<u>44.</u>	<u>11.</u>	<u>10.</u>				
	<u>236 "</u>	<u>30.</u>	<u>11.</u>	<u>1.</u>	<u>13.</u>				
	<u>241 "</u>	<u>15.</u>	<u>5.</u>	<u>4.</u>	<u><5.</u>				
	<u>242 "</u>	<u>5.</u>	<u>1.</u>	<u>1.</u>	<u>7.</u>				
	<u>247 "</u>	<u>41.</u>	<u>18.</u>	<u>11.</u>	<u>13.</u>				
	<u>248 "</u>	<u>33.</u>	<u>9.</u>	<u>3.</u>	<u><5.</u>				
	<u>253 "</u>	<u>80.</u>	<u>38.</u>	<u>6.</u>	<u><5.</u>				
	<u>254 "</u>	<u>32.</u>	<u>10.</u>	<u>6.</u>	<u><5.</u>				
	<u>259 "</u>	<u>113.</u>	<u>34.</u>	<u>6.</u>	<u>14.</u>				
	<u>260 "</u>	<u>14.</u>	<u>2.</u>	<u>1.</u>	<u>20.</u>				
	<u>265 "</u>	<u>69.</u>	<u>16.</u>	<u>4.</u>	<u>9.</u>				
	<u>266 "</u>	<u>21.</u>	<u>4.</u>	<u>2.</u>	<u>9.</u>				
	<u>271 "</u>	<u>38.</u>	<u>12.</u>	<u>6.</u>	<u><5.</u>				
	<u>272 "</u>	<u>26.</u>	<u>6.</u>	<u>6.</u>	<u><5.</u>				
	<u>277 "</u>	<u>75.</u>	<u>39.</u>	<u>6.</u>	<u><5.</u>				
	<u>278 "</u>	<u>15.</u>	<u>7.</u>	<u>4.</u>	<u>33.</u>				
	<u>283 "</u>	<u>66.</u>	<u>19.</u>	<u>12.</u>	<u>10.</u>				
	<u>284 "</u>	<u>39.</u>	<u>50.</u>	<u>1.</u>	<u>59.</u>				

date completed <u>March 15/79</u>	chemist <u>G.W. & C.K.</u>	approved <u>D. Mackey</u>
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samples to be filed ☐ returned ☐

put estimates on sample bags

• forward top 3 copies with samples to COPPER CLIFF
PROCESS TECHNOLOGY BUILDING
ANALYTICAL SERVICES LABORATORY

• retain pink copy

MISCELLANEOUS ASSAY REPORT

submitted by		charge number		date	
department			location		
program description					

lab no.	sample description	analysis required							
		Cu	Ni	Zn	Al				
	289 Soil	48.	8.	8.	10.				
	290 "	20.	4.	10.	<5.				
	295 "	55	28.	10.	9.				
	296 "	40	20	22.	16.				
	301 "	69	25.	25.	<5.				
	302 "	22.	6.	19.	<5.				
	307 "	107.	72.	13.	10.				
	308 "	34.	14.	5.	<5.				
	313 "	83.	1.	40	<5.				
	314 "	55.	20.	12.	<5.				
	319 "	80.	50.	16.	16.				
	320 "	44.	26.	9	40.				
	865 "	13.	7.	3.	18.				
	866 "	8.	2.	3.	65.				
	871 "	34.	7.	3.	10.				
	872 "	46.	5.	8.	13.				
	877 "	50.	11.	3.	29.				
	878 "	13.	2.	4.	56.				
	883 "	80.	24.	18.	8.				
	884 "	47.	13.	6.	13.				
	889 "	46.	16.	12.	<5.				
	890 "	11.	6.	2.	6.				
	895 "	26.	10.	12.	<5.				
	896 "	5.	2.	1.	<5.				

date completed	March 15/79	chemist	C. K.	approved	<i>DM</i>
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MISCELLANEOUS ASSAY REPORT

submitted by	charge number	date
department		location
program description		

lab no.	sample description	analysis required													
		PPM													
		Cu	Ni	Zn	Al										
	901 Soil	112.	27.	5.	36.										
	902 "	44.	13.	11.	53.										
	907 "	61.	21.	5.	20.										
	908 "	32.	3.	5.	24.										
	913 "	77.	34.	6.	8.										
	914 "	32.	10.	4.	23.										
	919 "	72.	26.	9.	20.										
	920 "	28.	24.	4.	59.										
	925 "	28.	9.	3.	10.										
	926 "	29.	7.	3.	13.										
	931 "	71.	29.	10.	18.										
	932 "	26.	16.	2.	41.										
	937 "	53.	17.	11.	10.										
	938 "	44.	16.	5.	21.										
	943 "	116.	52.	53.	8.										
	944 "	63.	34.	6.	29.										
	949 "	40.	18.	15.	6.										
	950 "	24.	12.	3.	35.										
	955 "	20.	12.	9.	16.										
	956 "	17.	7.	3.	13.										
	961 "	78.	52.	14.	20.										
	962 "	42.	21.	2.	35.										
	967 "	55.	33.	10.	16.										
	968 "	44.	21.	4.	28.										

date completed <i>March 15/79</i>	chemist <i>C. K.</i>	approved <i>DM</i>
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MISCELLANEOUS ASSAY REPORT

submitted by		charge number		date	
department			location		
program description					

job no.	sample description	analysis required							
		PPM							
		Cu	Ni	Zn	Al				
	1083 Soil	65.	53.	32.	8.				
	1084 "	66.	57.	14.	10.				
	1089 "	47.	11.	3.	10.				
	1090 "	21.	3.	4.	13.				
	1095 "	41.	18.	12.	6.				
	1096 "	11.	5.	5.	23.				
	1101 "	111.	28.	29.	10.				
	1102 "	60.	17.	10.	26.				
	1107 "	19.	7.	8.	<5.				
	1108 "	5.	2.	2.	8.				
	1113 "	64.	36.	21.	11.				
	1114 "	44.	41.	6.	23.				
	1119 "	129.	35.	4.	33.				
	1120 "	37.	9.	3.	63.				
	1125 "	78.	51.	5.	15.				
	1126 "	48.	18.	3.	21.				
	1131 "	69.	14.	6.	18.				
	1132 "	17.	4.	5.	26.				
	1137 "	131.	47.	44.	14.				
	1138 "	47.	14.	3.	44.				
	1143 "	66.	23.	7.	15.				
	1144 "	23.	7.	1.	26.				
	1149 "	78.	50.	18.	10.				
	1150 "	40.	23.	3.	26.				

date completed	March 15/79	chemist	C. K.	approved	DM
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ANALYTICAL SERVICES LABORATORY

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submitted by	charge number	date
department	location	
program description		

[illegible]

date completed *March 15/79* | chemist *C. K.* | approved *DM*

samples to be filed ☐ returned ☐

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PROCESS TECHNOLOGY BUILDING
ANALYTICAL SERVICES LABORATORY
- retain pink copy

2. MOE EXTRACTOR VERSUS INCO SHAKE TEST

AMMONIUM ACETATE pH 4.8

FIGURE

I	COPPER
II	NICKEL
III	ZINC

FIGURE I

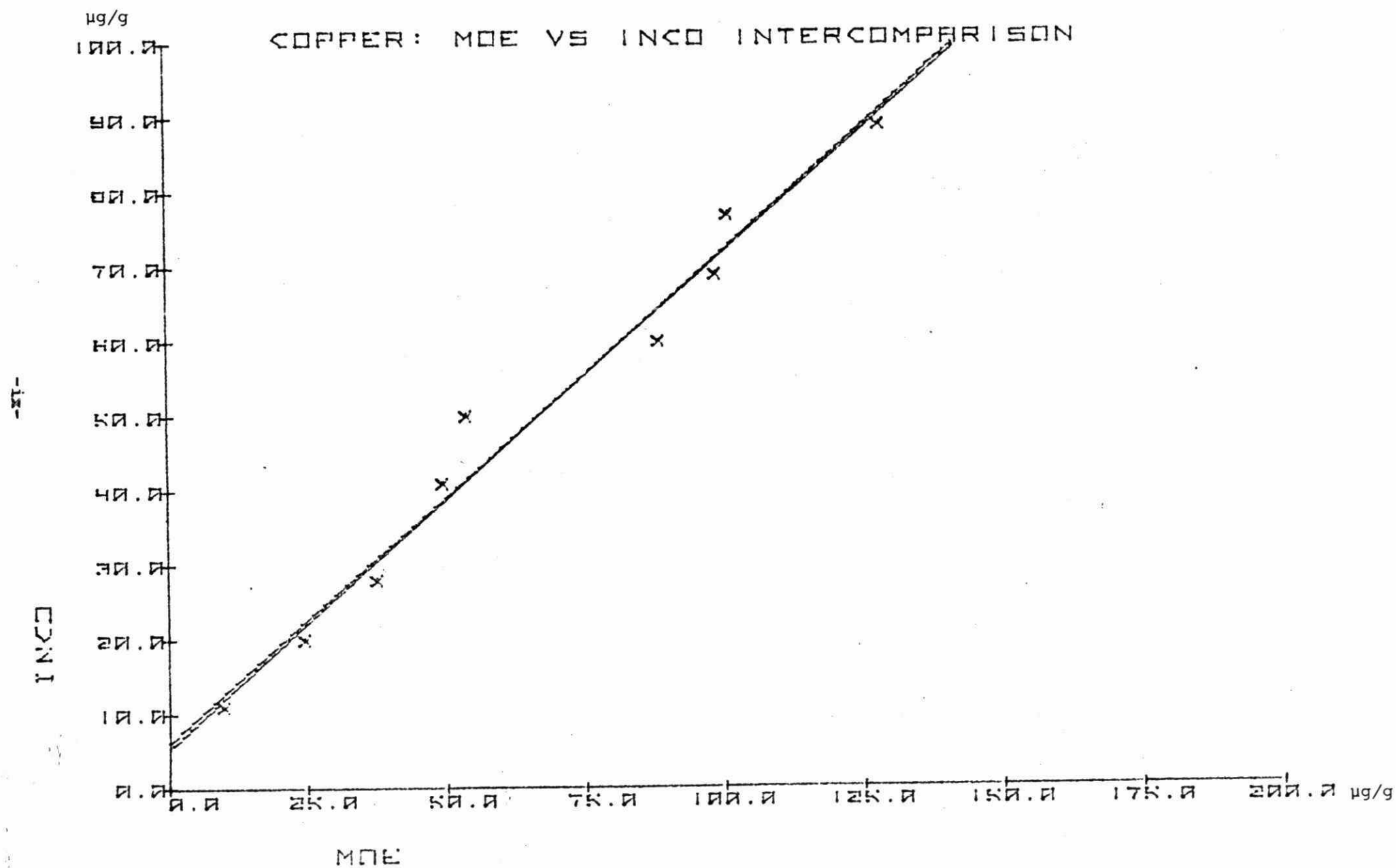


FIGURE II

NICKEL: MOE VS INCO INTERCOMPARISON

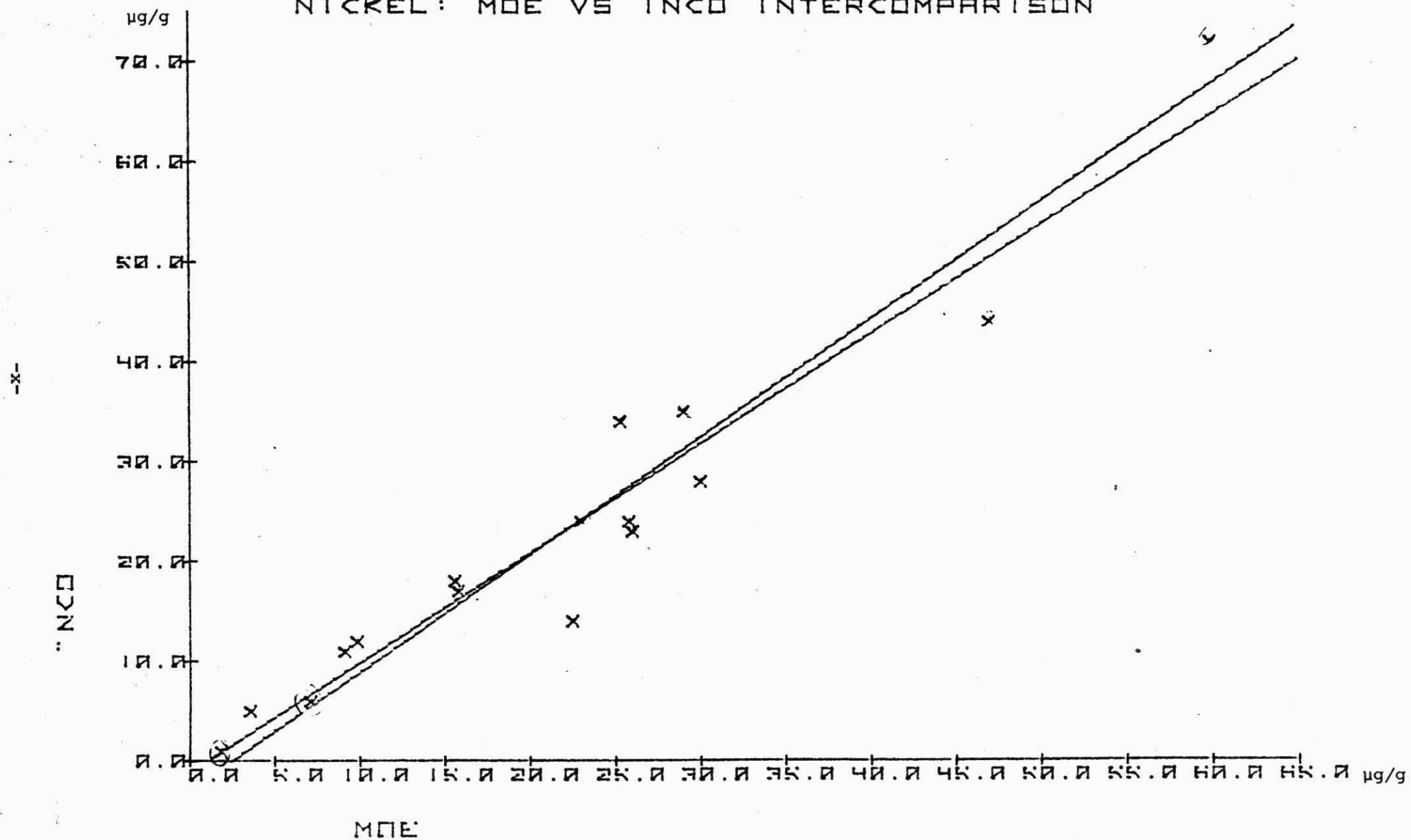


FIGURE III

ZN: INCO VS MOE INTERCOMPARISON,

Ammonium Acetate

$$Y = -1.568 + 1.419 * X$$

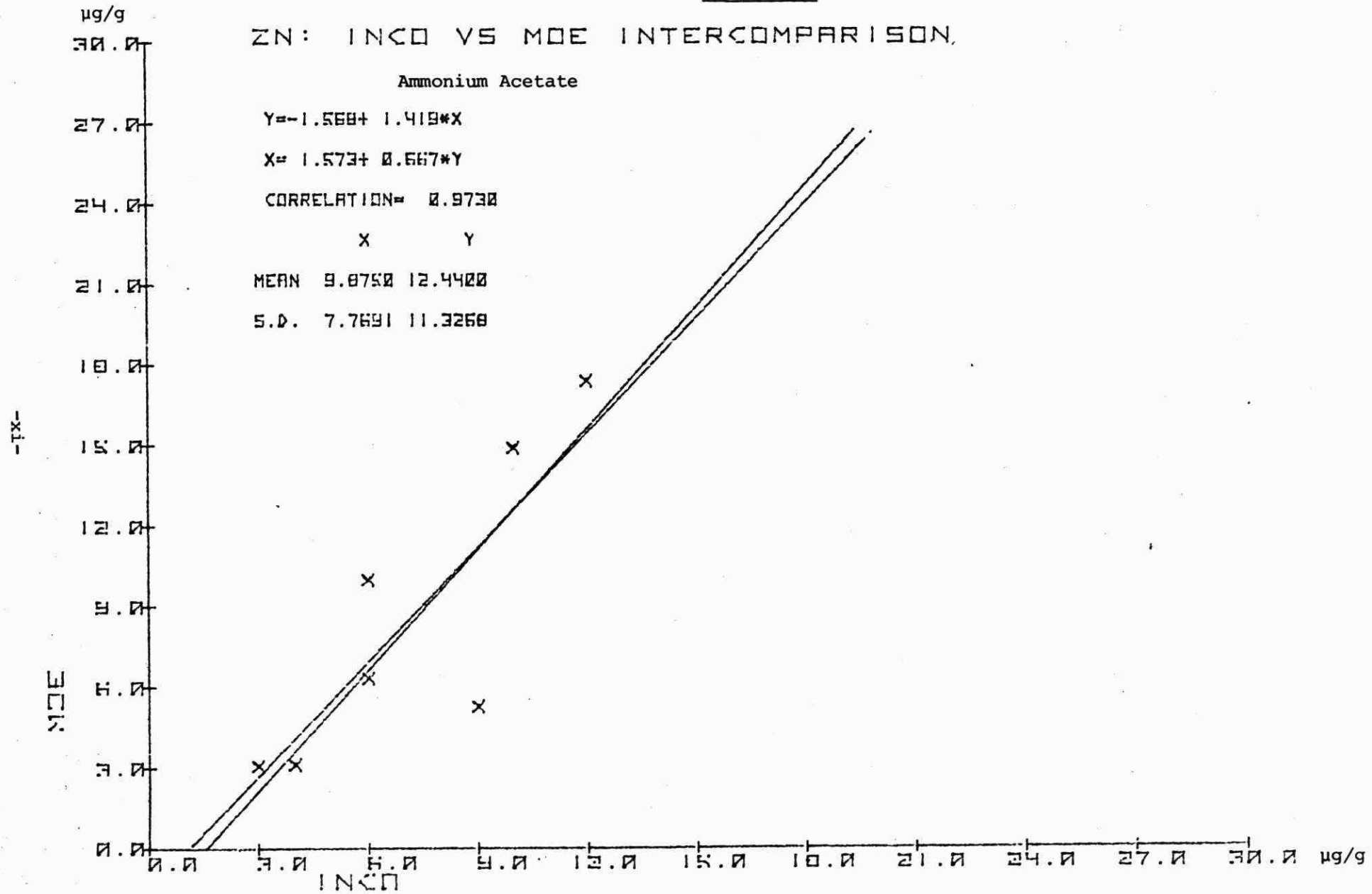
$$X = 1.573 + 0.667 * Y$$

CORRELATION = 0.9730

X Y

MEAN 9.8750 12.4400

S.D. 7.7691 11.3268



3. SOLID: EXTRACTANT RATIO

MECHANICAL VACUUM EXTRACTOR

AMMONIUM ACETATE pH 4.8

1:4 versus 1:10

FIGURE

IV	COPPER
V	NICKEL
VI	ZINC
VII	COPPER (1:4 versus 1:16)

COMPLETENESS OF EXTRACTION

VIII SOLID: AMMONIUM ACETATE RATIO
COPPER AND NICKEL

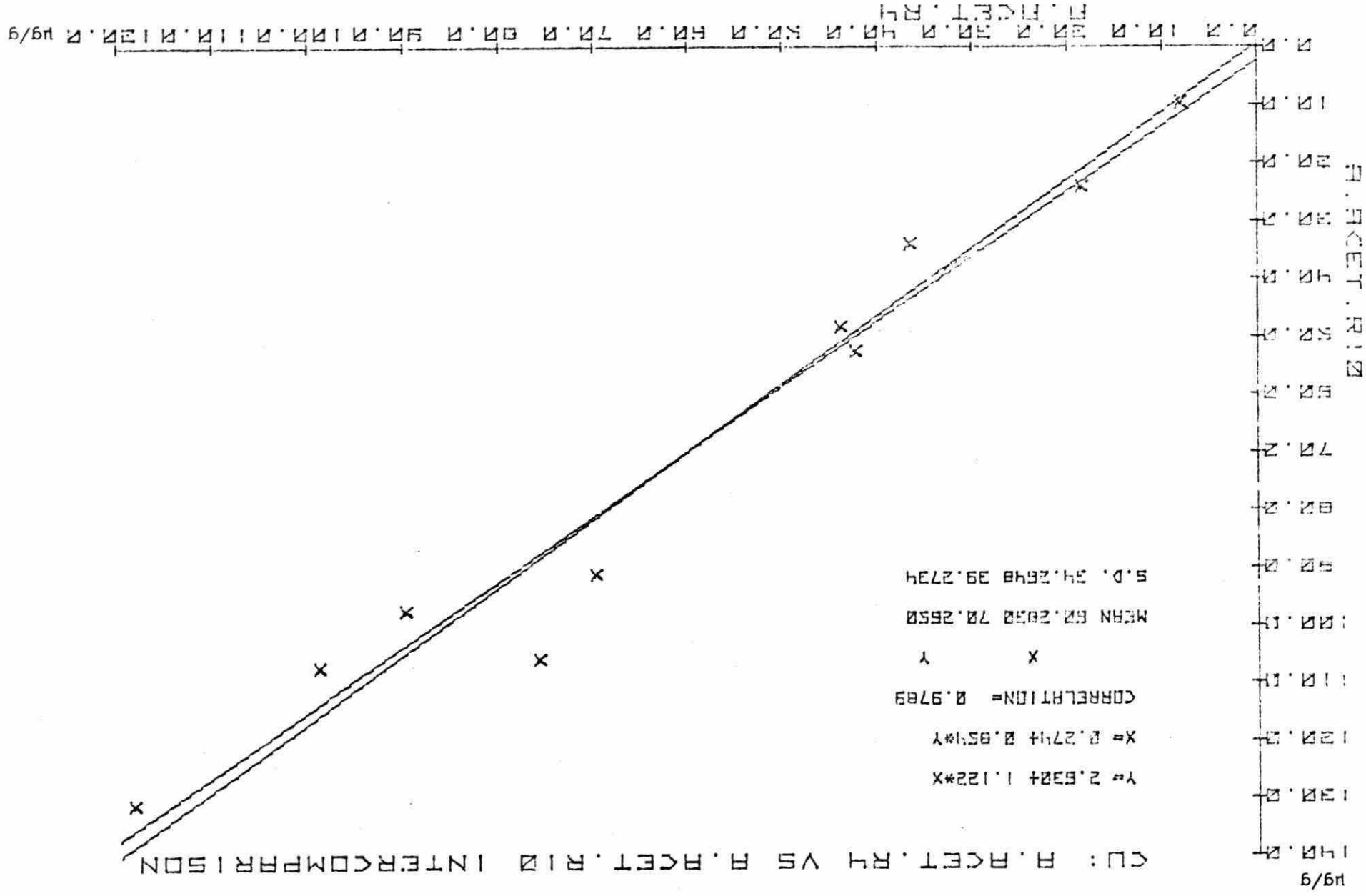


FIGURE IV

FIGURE V

N1: A.ACET.R4 VS A.ACET.R10 INTERCOMPARISON

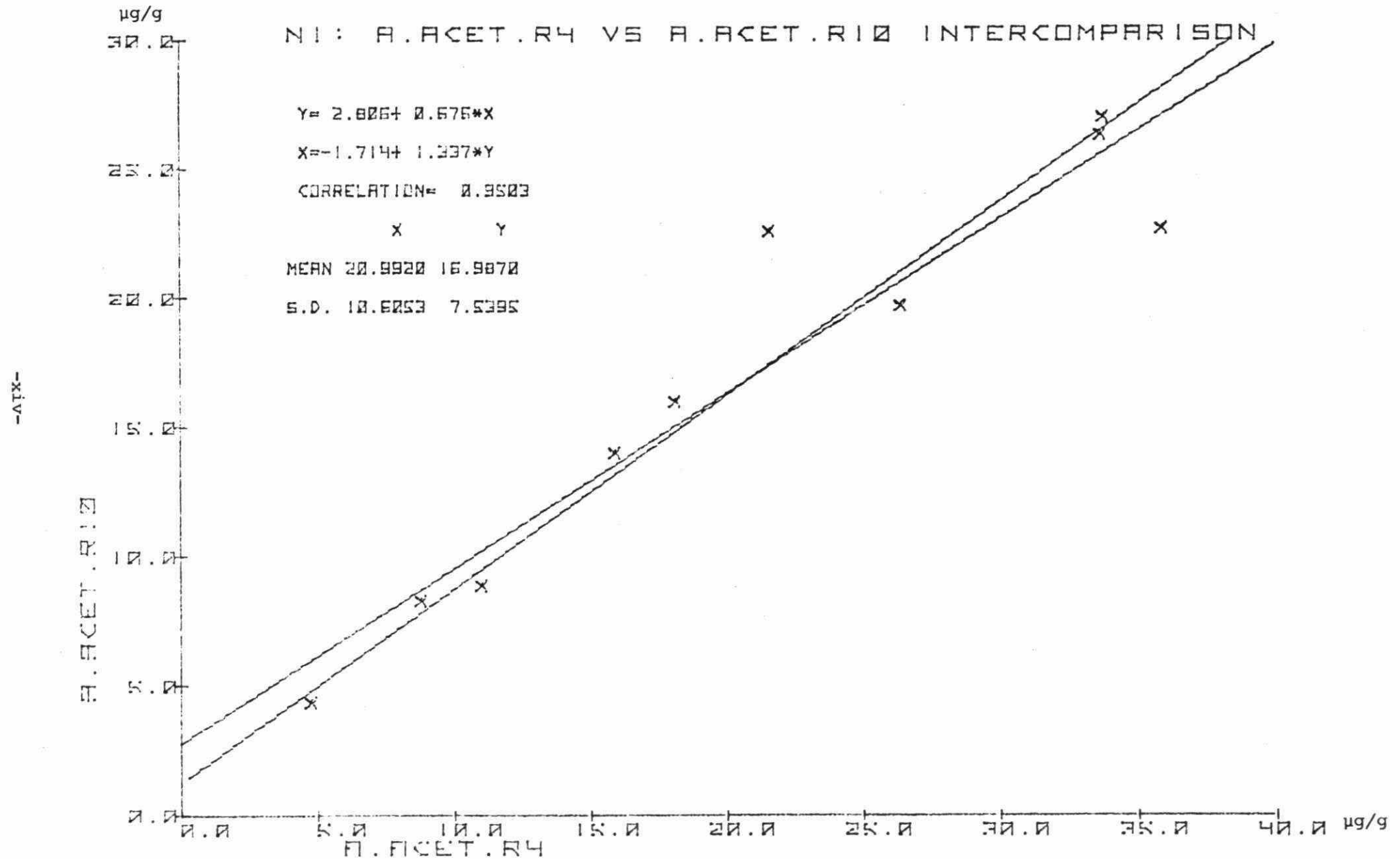
$$Y = 2.806 + 0.675 * X$$

$$X = -1.714 + 1.337 * Y$$

CORRELATION = 0.9503

MEAN 20.9920 16.9870

S.D. 10.6053 7.5395



ZN: R. P.C.E.T. RY VS R. P.C.E.T. R10 INTERCOMPARISON

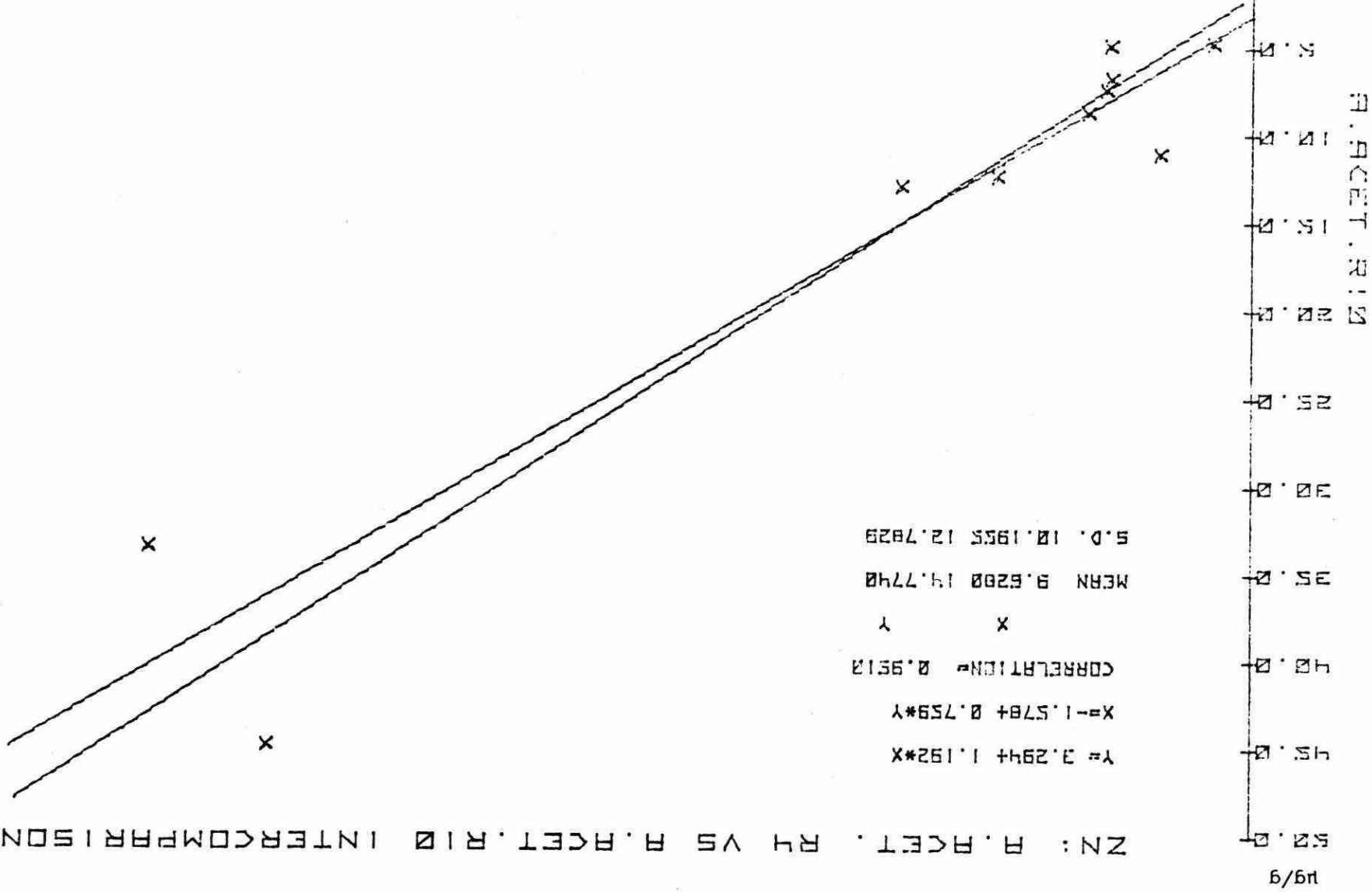


FIGURE VI

μg/g 5.0 10.0 15.0 20.0 25.0 30.0 35.0 40.0 45.0 50.0
 R. P.C.E.T. R10
 5.0 10.0 15.0 20.0 25.0 30.0 35.0 40.0 45.0 50.0
 R. P.C.E.T. RY
 6/61

FIGURE VII

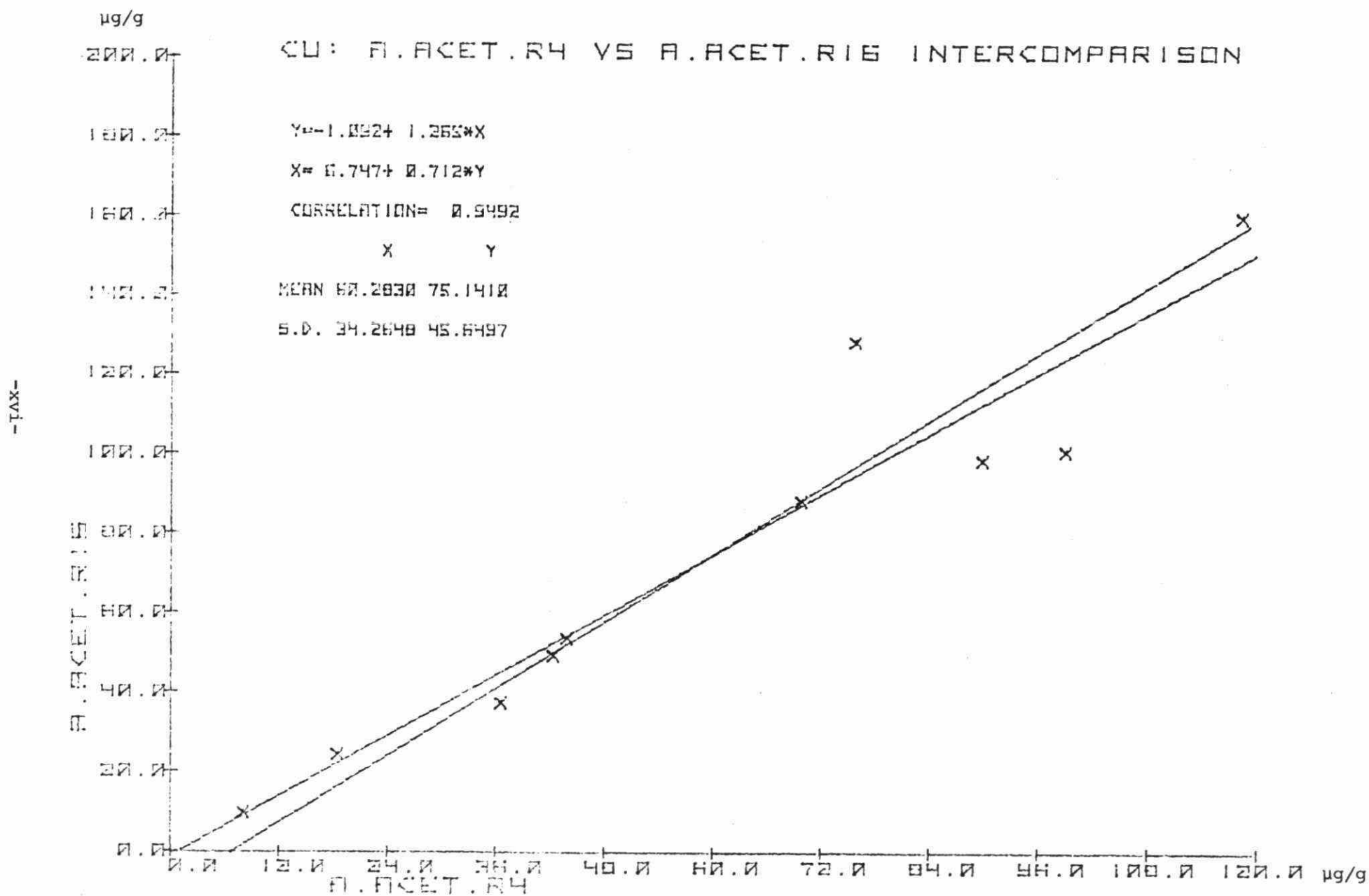
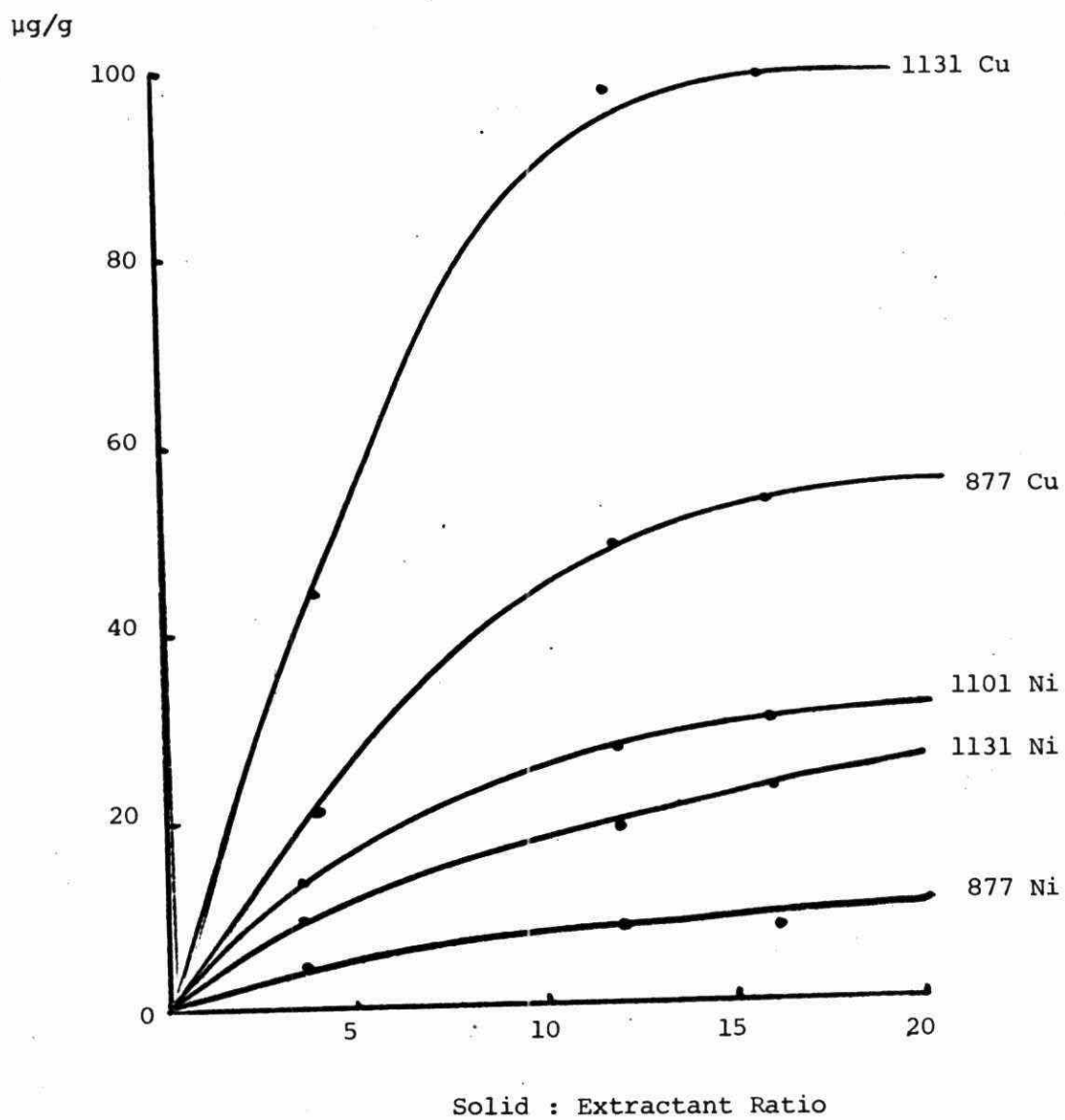


FIGURE VIII

Solid - Ammonium Acetate Ratio

Copper and Nickel



4. DIGESTED (HCl/HNO_3) VERSUS UNDIGESTED (AS-IS)

AMMONIUM ACETATE EXTRACTS

FIGURE

IX COPPER

X NICKEL

FIGURE IX

µg/g
DIG

Digested versus As-Is
Ammonium Acetate
Copper

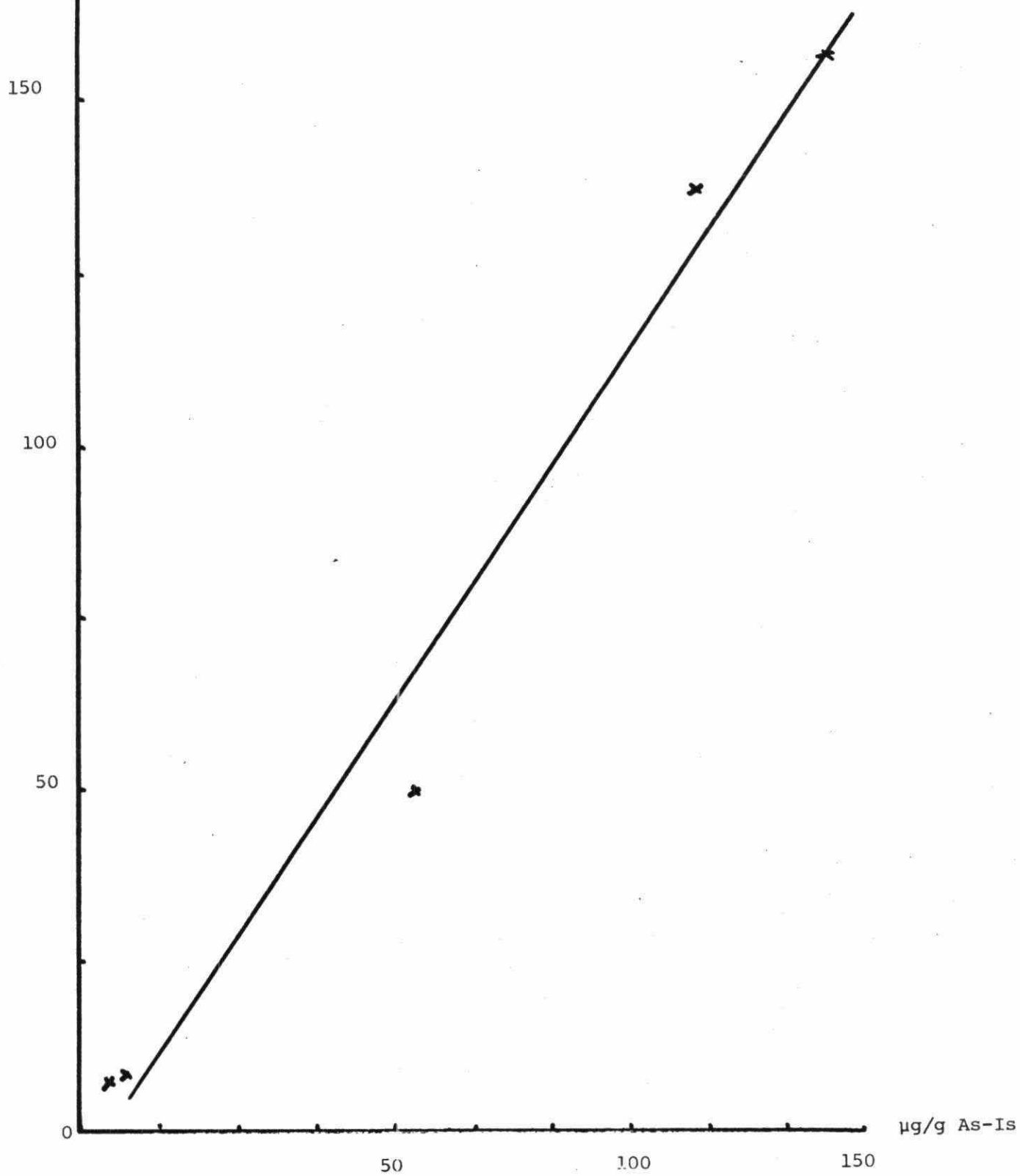
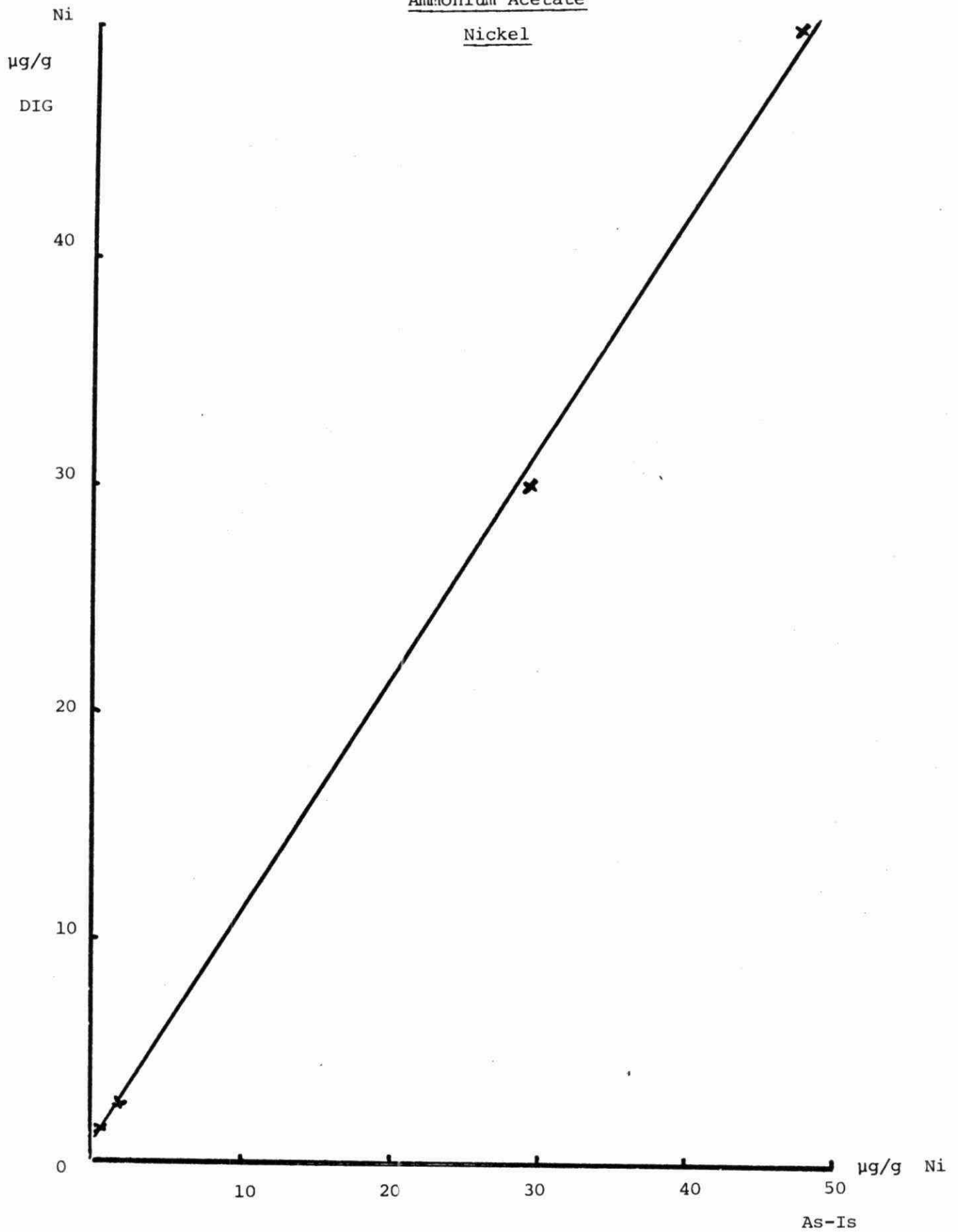


FIGURE X
Digested versus As-Is
Ammonium Acetate
Nickel



5. AMMONIUM ACETATE pH 4.8 VERSUS DTPA

MECHANICAL VACUUM EXTRACTOR

FIGURE

XI COPPER

XII NICKEL

FIGURE XI

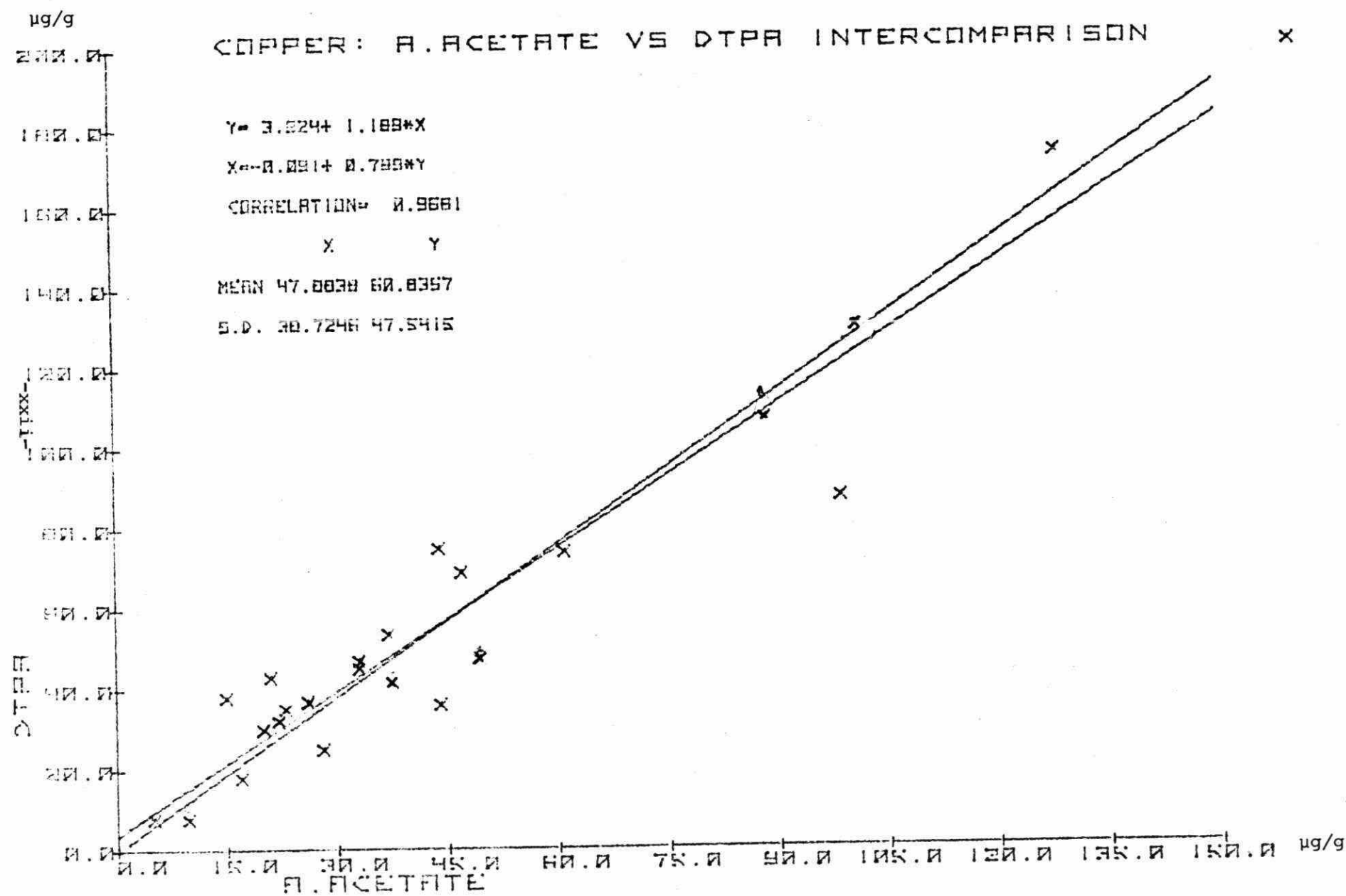
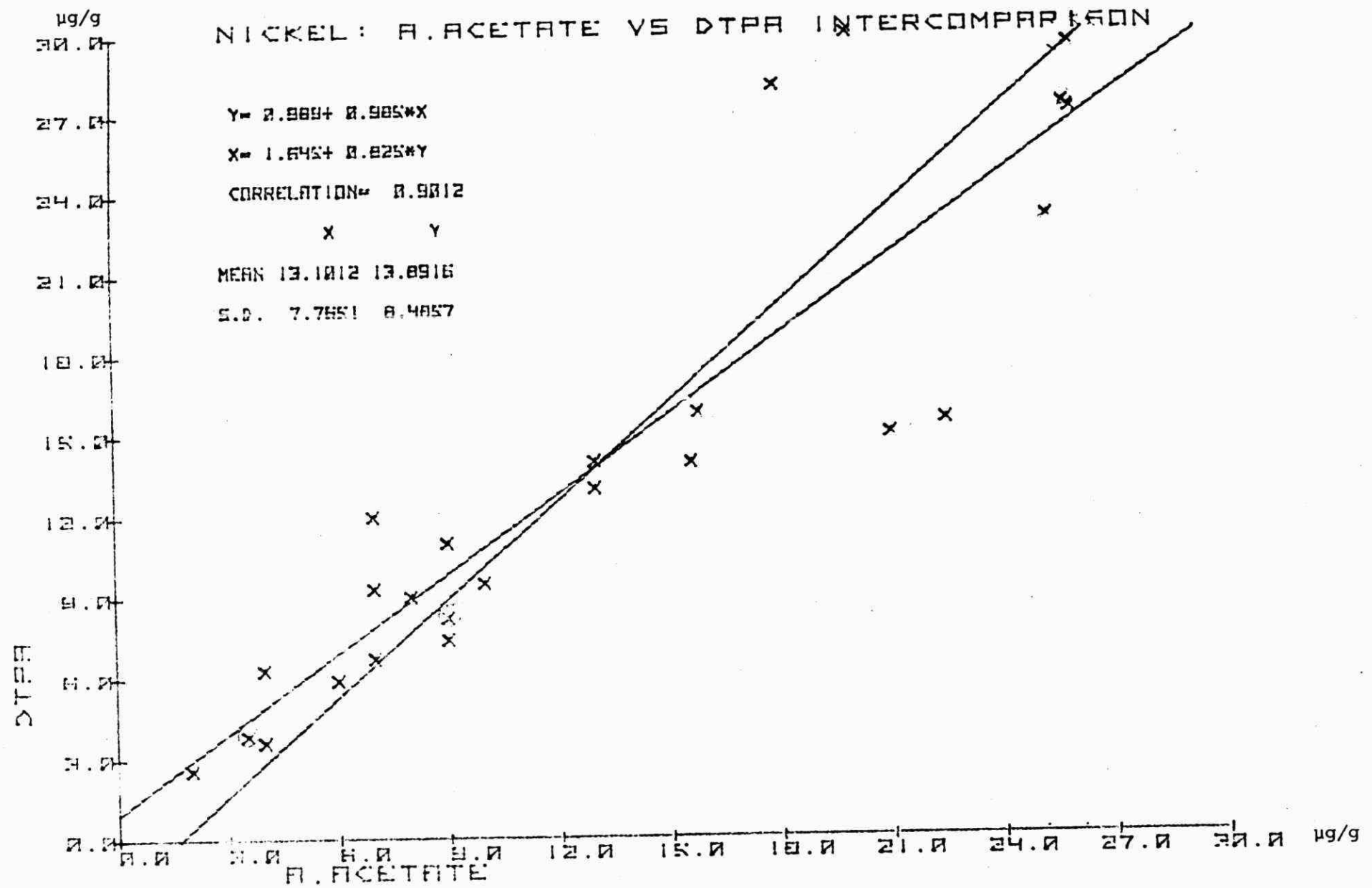


FIGURE XII



6. SOLID: DTPA RATIO

MECHANICAL VACUUM EXTRACTOR

FIGURE

XIII COPPER

XIV NICKEL

FIGURE XIII

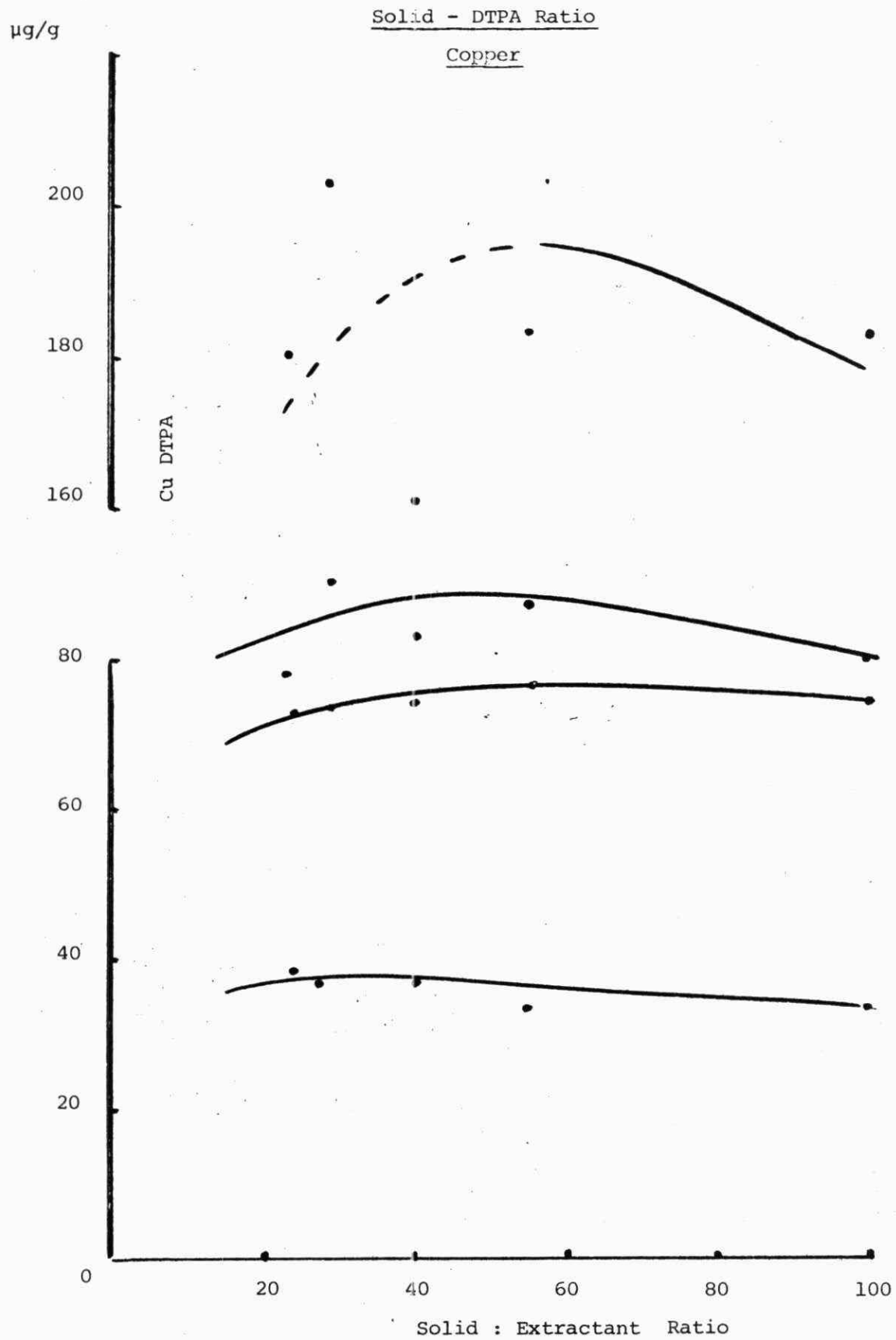
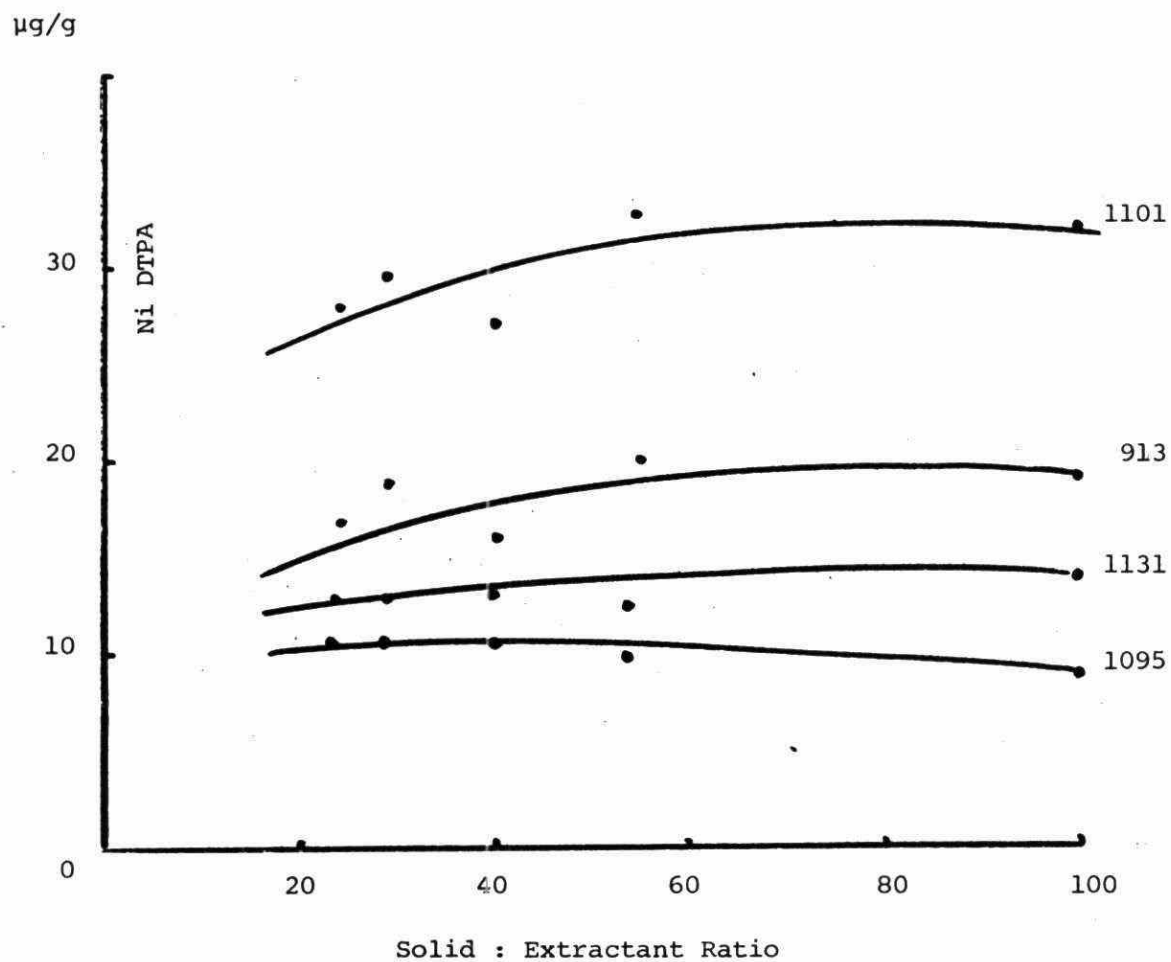


FIGURE XIV

Solid : DTPA Ratio

Nickel



7. EXTRACTANTS FOR ALUMINUM

FIGURE	<u>INTERCOMPARISONS</u>
XV	INCO VERSUS MOE - AMMONIUM ACETATE
XVI	KCl VERSUS AMMONIUM ACETATE
XVII	AMMONIUM ACETATE 1:4 versus 1:10
	<u>AGREEMENT BETWEEN RUNS</u>
XVIII	KCl EXTRACTABLE
XIX	CuCl ₂ EXTRACTABLE
	<u>ORGANIC ALUMINUM: CuCl₂-KCl</u>
XX	ORGANIC ALUMINUM VERSUS L01

FIGURE XV

Al: INCO versus MOE

Ammonium Acetate

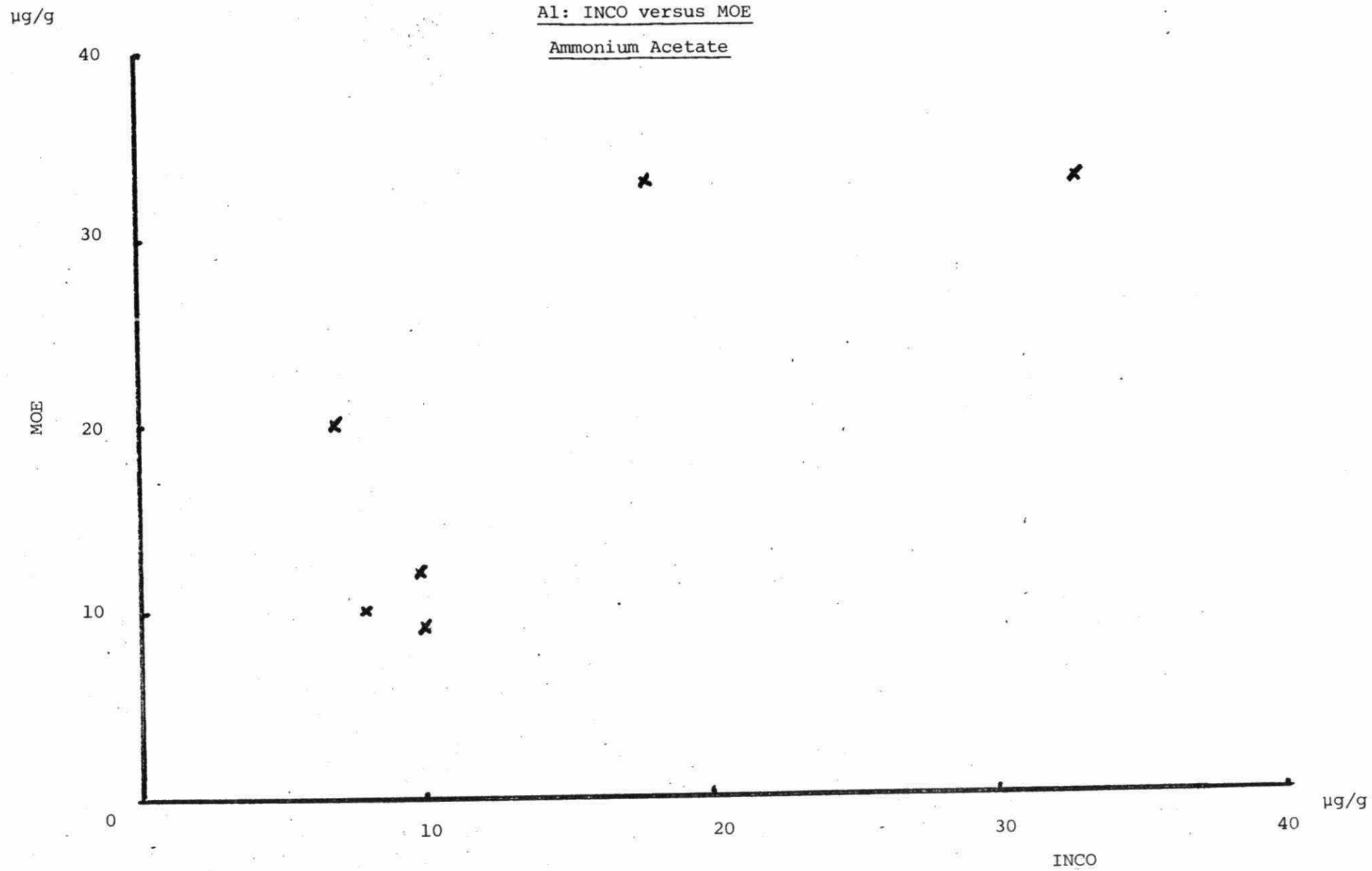


FIGURE XVI

Extractable Aluminum
KCl versus Ammonium Acetate

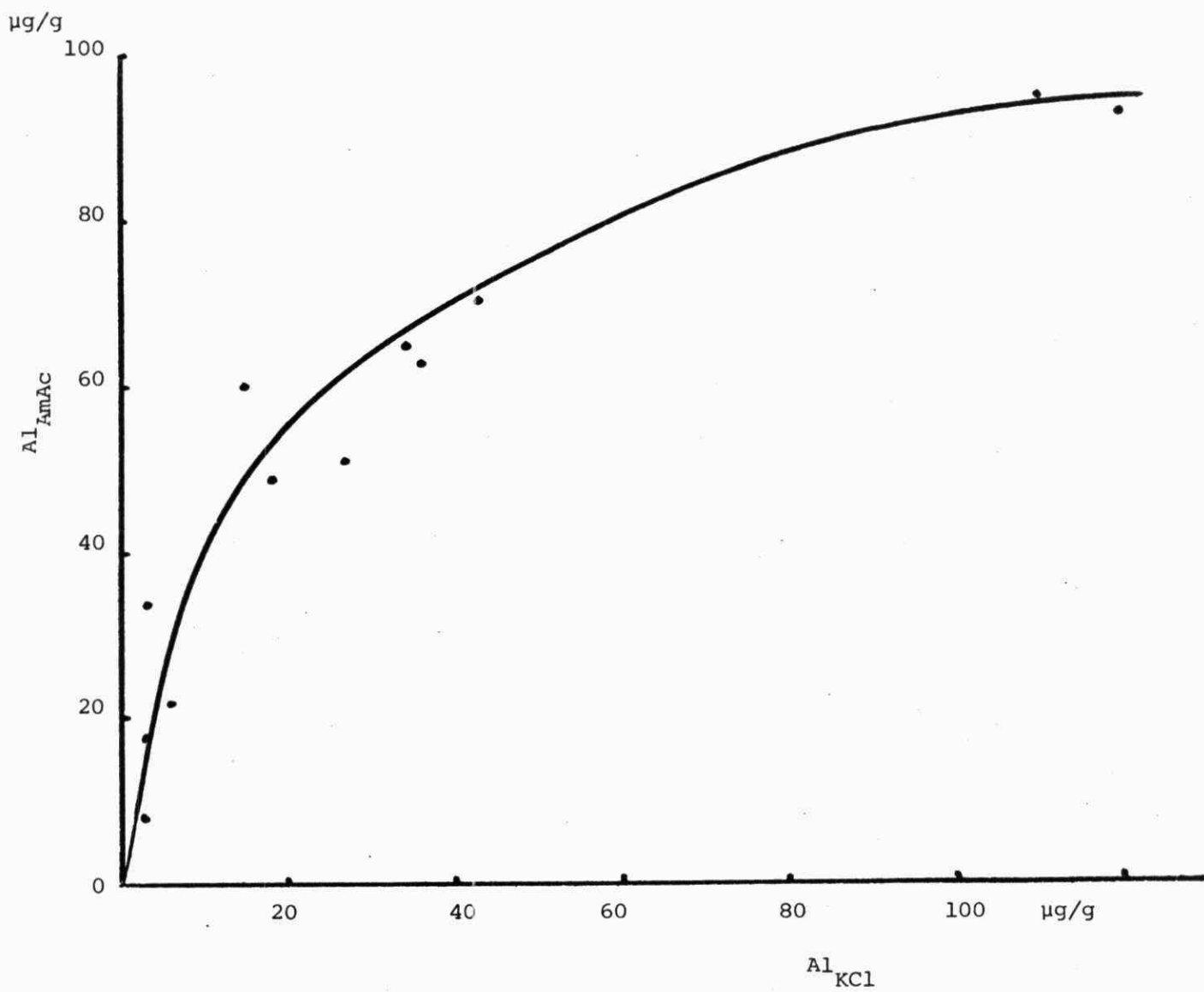


FIGURE XVII

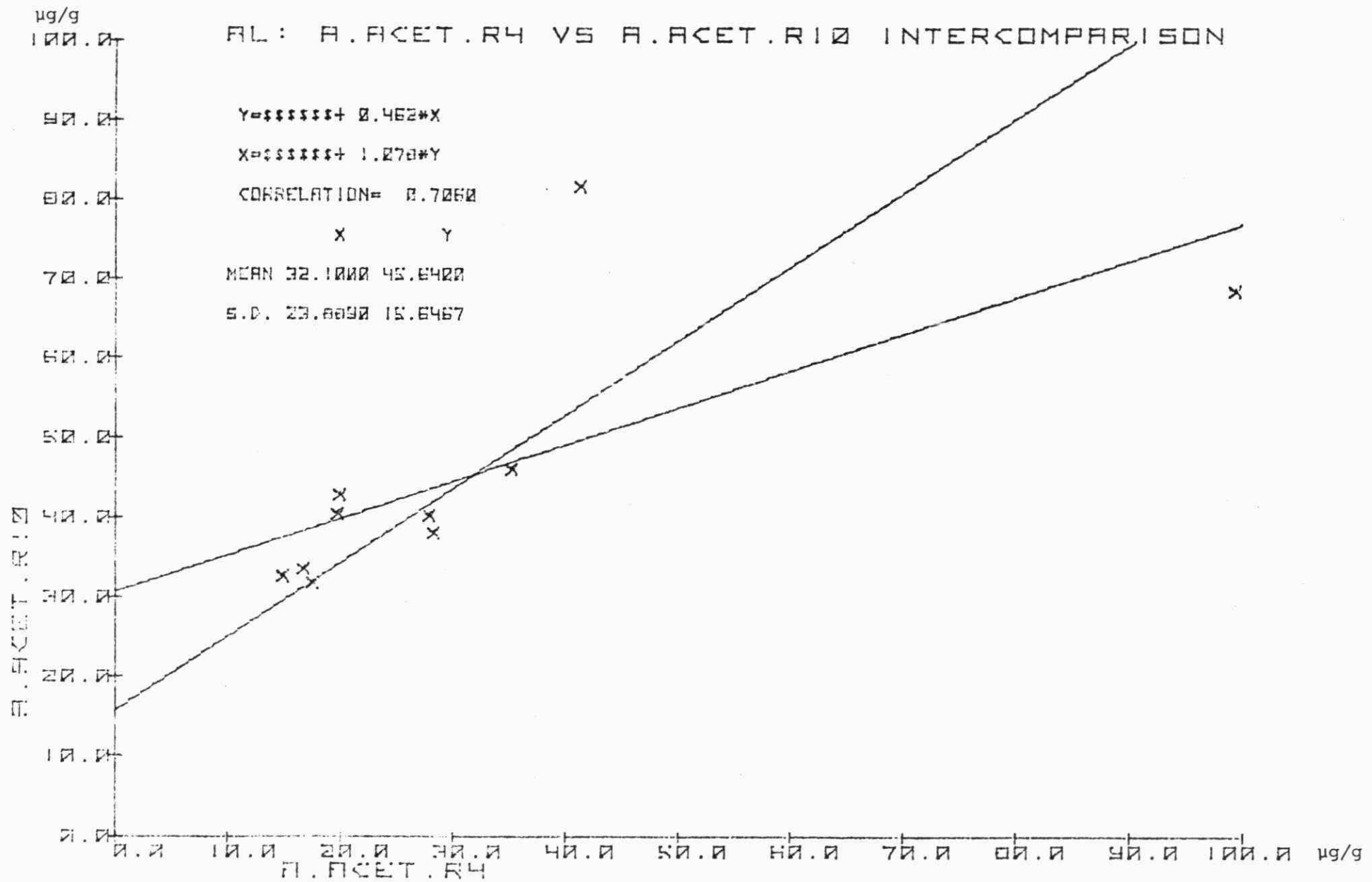


FIGURE XVIII
KCl Extractable Aluminum
Agreement Between Runs

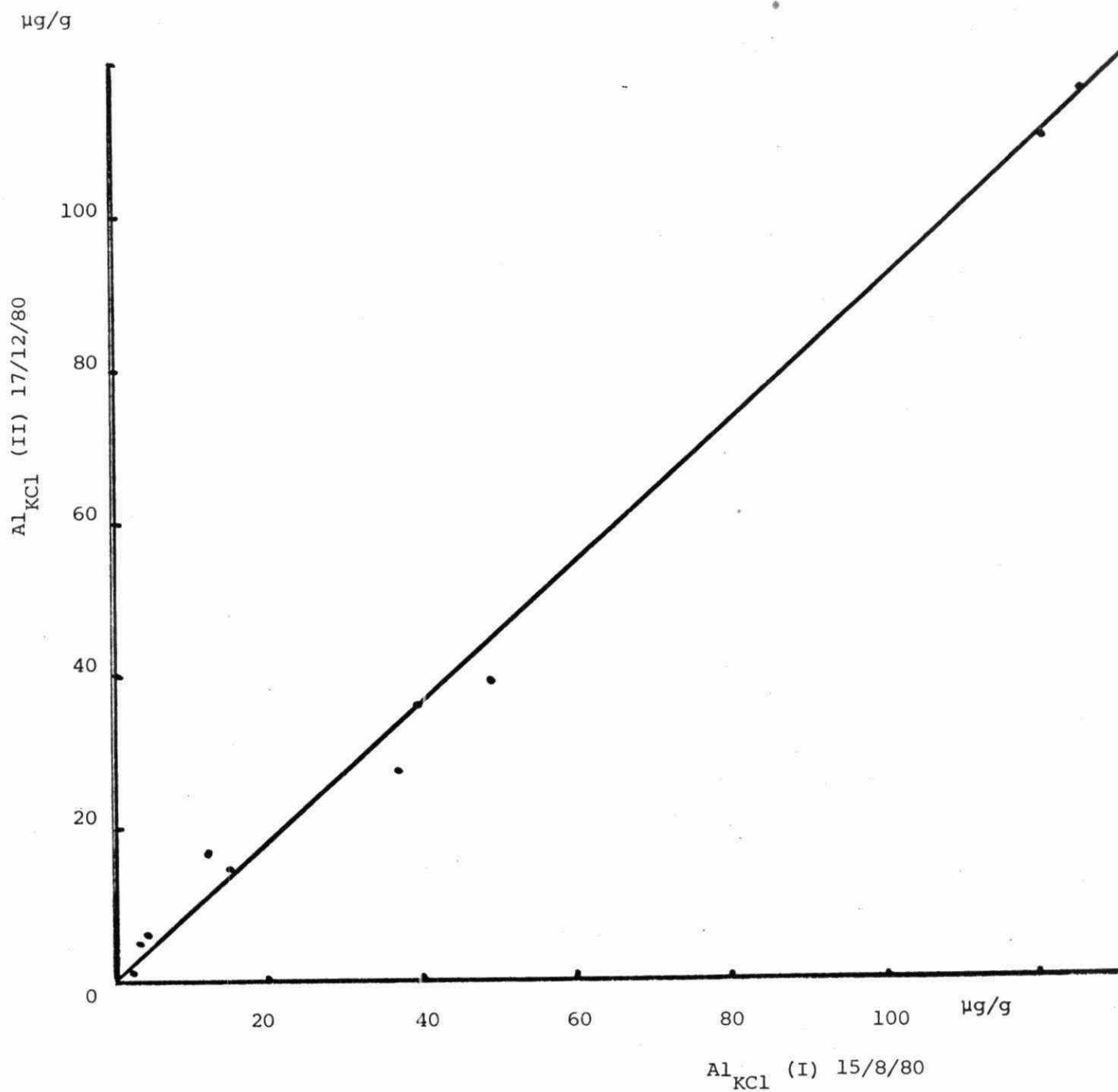


FIGURE XIX

CuCl₂ Extractable Aluminum
Agreement Between Runs

μg/g

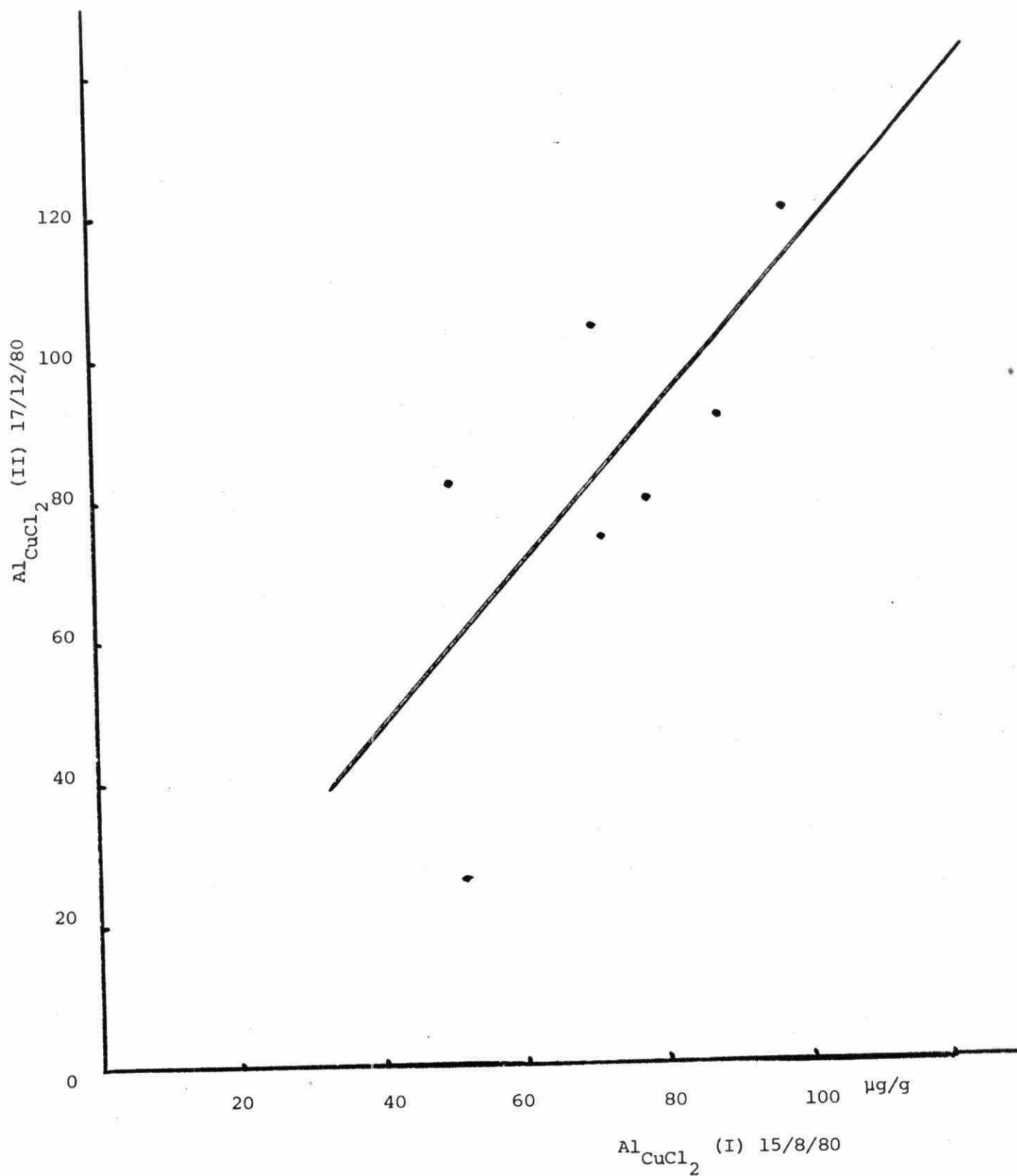
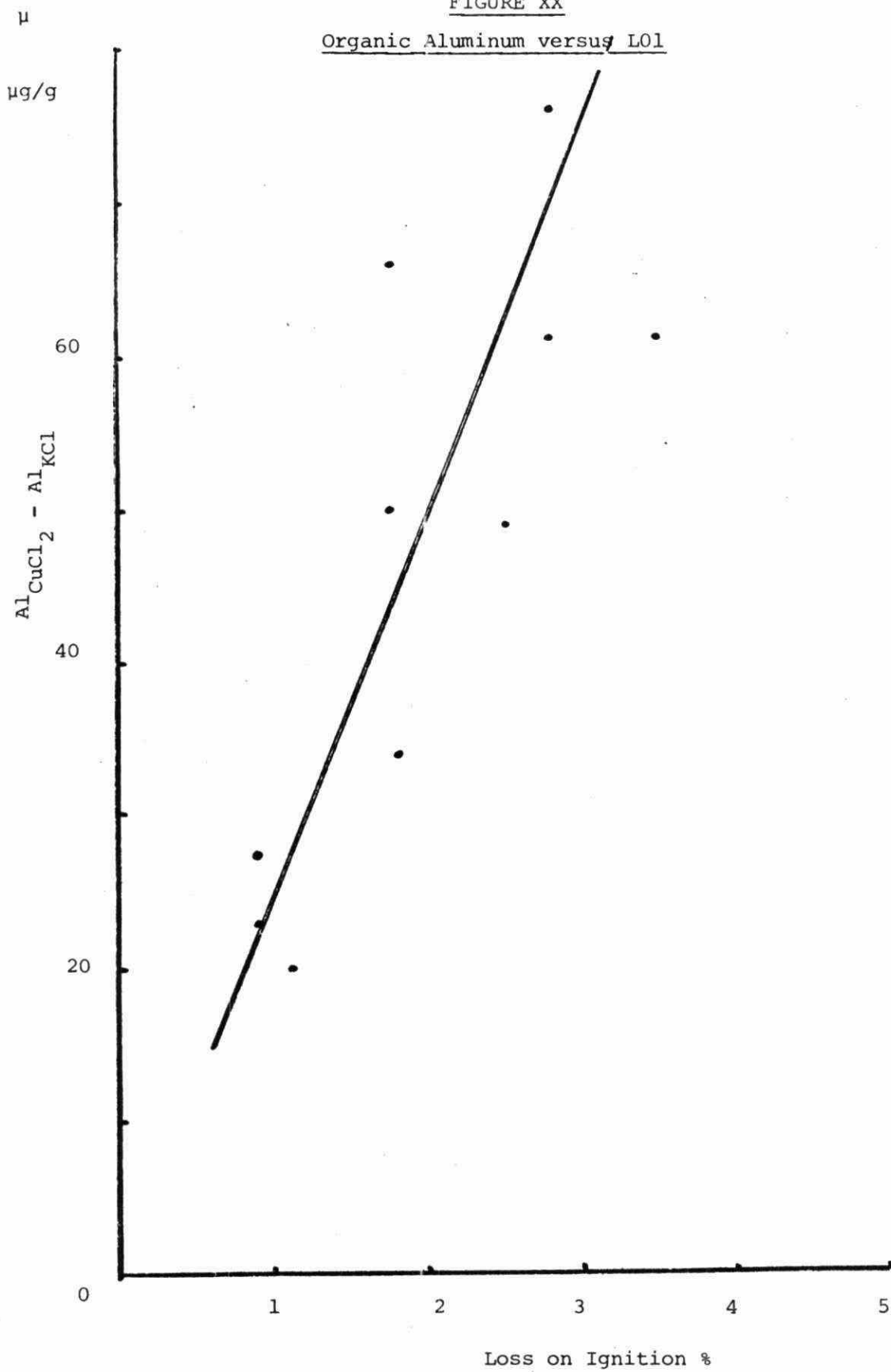


FIGURE XX

Organic Aluminum versus L01



8. MECHANICAL VACUUM EXTRACTOR

FIGURE

XXI GENERAL ASSEMBLY

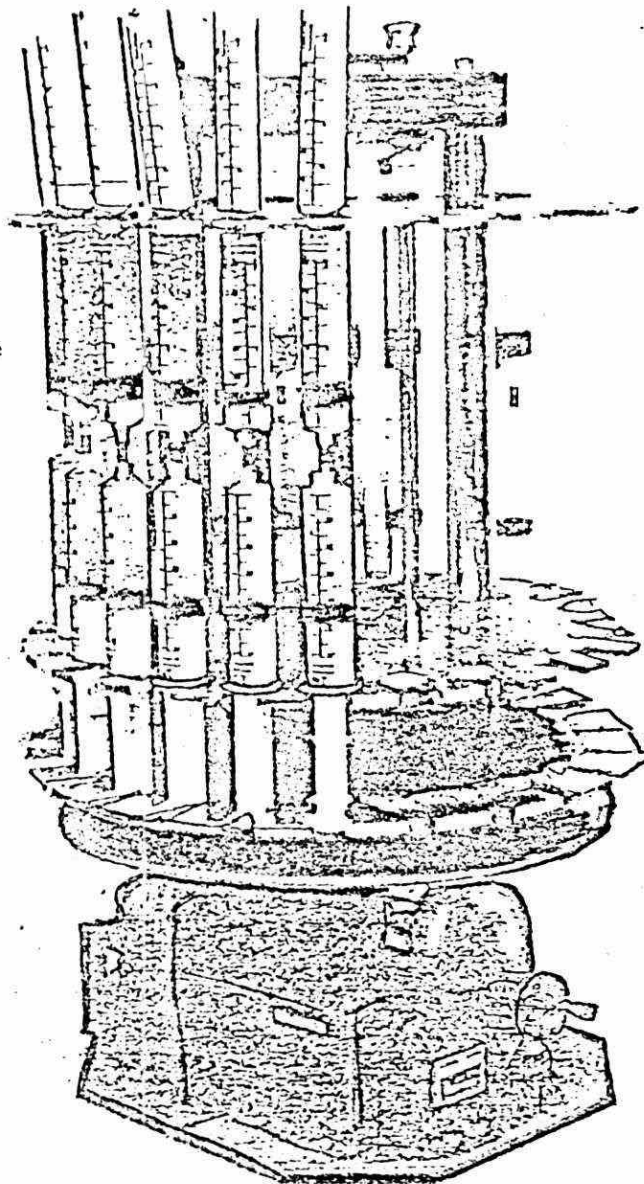
XXII SYRINGE ARRANGEMENT

Figure XXI

Upper syringe
(Extractant)

Middle syringe
sample

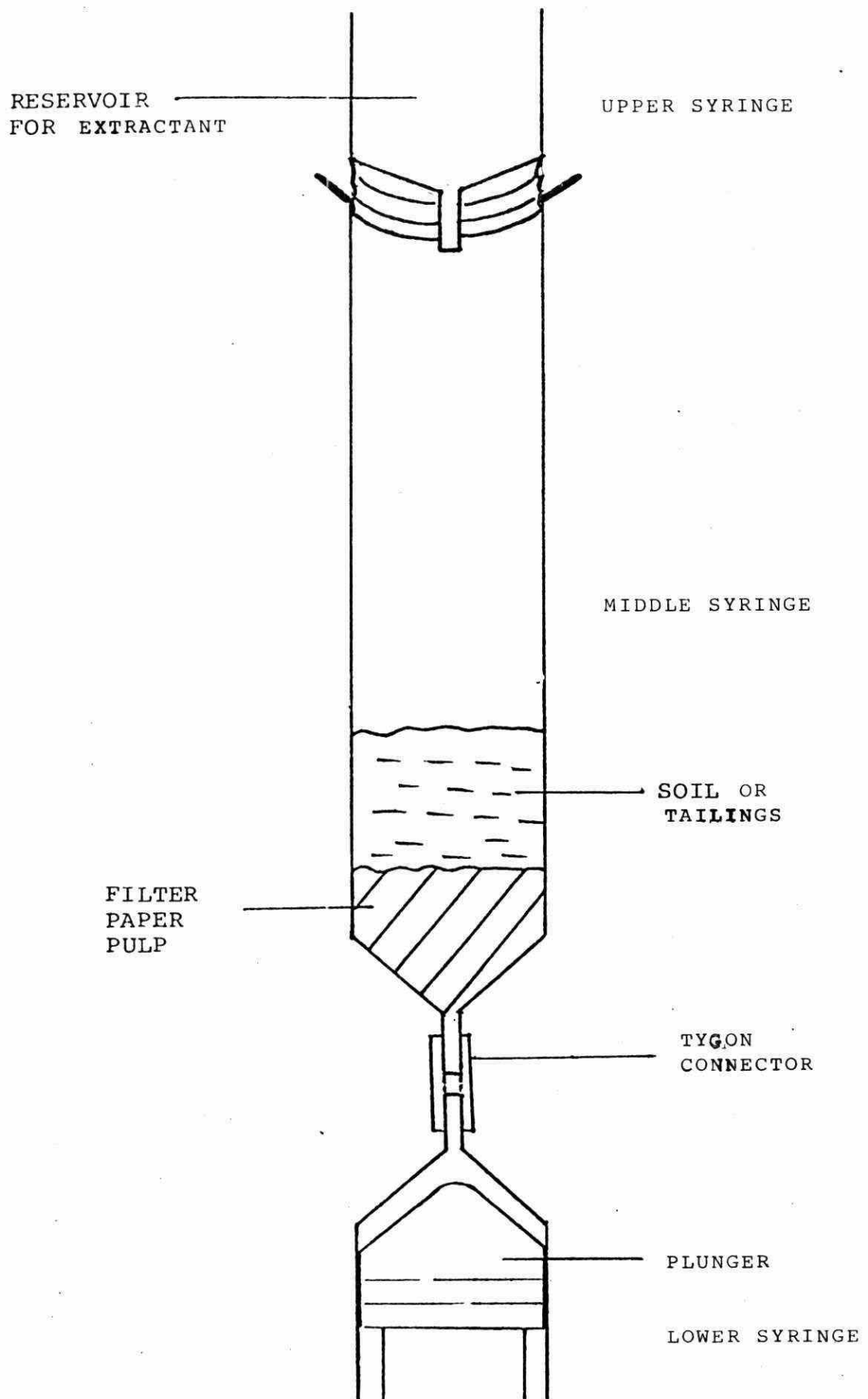
Lower syringe
extract



MECHANICAL VACUUM EXTRACTOR

Concept Engineering Inc.
1800 Center Park Road
South Industrial Park
Lincoln, Nebraska 68502

Figure XXII



ARRANGEMENT OF SAMPLE-EXTRACTANT

1887
D-18
D-37
1887
1887